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CONTENTS.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Saturday December 27, 1913.

VOL XVI.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

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CONTENTS.

Anatomy. — *"On the Metamorphosis of Amphioxus lanceolatus"*.

By Prof. J. W. VAN WIJHE.

(Communicated in the meeting of April 25, 1913).

Amphioxus still continues to be one of the most interesting objects for the morphology of vertebrates, though the time is past in which he was almost considered as their ancestor. It is now pretty well generally admitted, that Amphioxus is not the grandfather of vertebrates. It has appeared that his organisation deviates so strongly from what must be regarded as the original type, that some morphologists do not take him for a genuine grand-father, but for a step-grand-father, who, in reality, does not belong at all to the family, and only confuses its relations.

There have been morphologists, and perhaps there are still some, whose theories appeared to be so much at variance with the organisation of Amphioxus, that they have proposed to strike him out from the group to which vertebrates belong, and if they had been able would willingly have brought him back to the group of snails, to which PALLAS in his time supposed him to belong, and for that reason gave him the name of Limax lanceolatus.

Though these investigators could not deny, that Amphioxus is affined to vertebrates, in order to save their theories, they were obliged to declare, that this relation is such a distant one, that it is certainly not necessary to make allowance for his organisation.

When however this organisation, both anatomically and embryologically [1]), became better known, it appeared more and more that Amphioxus shows indeed in many respects a very primitive organisation, which must be taken as point of issue for that of the higher vertebrates, whilst it presents, in other respects, such peculiar phenomena, that these must doubtlessly be regarded as deviations from types, that are represented among vertebrates.

I shall by-and-by discuss one of the most remarkable deviations. It is the placing of the mouth and the gill-slits in the larva before the metamorphosis.

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[1]) How slowly our knowledge in this respect increases may appear from the fact, that the celebrated morphologist BALFOUR was in 1882 still of opinion that Amphioxus should possess no ventral nerve-roots, whilst, with regard to the dorsal nerve-roots, one is still searching where the cells lie, which, in vertebrates, form the spinal ganglia. I have discovered under the atrial-epithelium that covers the liver, the intestine and gut an enormously large number of splendid multipolar ganglion-cells, whose axis-cylinder runs along the dorsal nerve-roots to the spinal cord.

After the expiration of the embryonal period one distinguishes three stages in the development of Amphioxus: 1st the stage of the larval growth; 2nd the stage of the metamorphosis; 3rd the stage of the postlarval growth.

At the beginning of the first stage the larva is 1 m.m. long; at the end of it it has reached a length of between 4 and 5 m.m. At the beginning of this period only the first gill-slit is formed, behind it are gradually developed a second, a third etc. till a number of 14 to 16 is reached. All these gill-slits belong morphologically to the left side of the body; those of the right side appear only in the period of the metamorphosis. During the stage of the larval growth constantly new muscle-segments (myotomes) are added to the posterior part of the body, but at the beginning of the metamorphosis this number is already complete. The animal is then only 4 to 5 m.m. long, but it posesses already the complete number of 60 muscle-segments with the nerves appertaining to them, which are also found in the full-grown animal which is almost a finger long.

During the comparatively long time of the metamorphosis, which is divided by WILLEY into 8 subdivisions, astonishing changes take place, not so much in the nervous or muscular system (with the exception of the gill-muscles), but especially in the shape and the placing of the mouth and of the gill-slits.

The animal does not grow during the metamorphosis, for its length amounts, both at the beginning and at the end, to between 4 and 5 m.m.[1]). Differences in length do not indicate here a further development. A larva that is half a millimeter longer than another needs not be older than the latter, but is often younger. It has even appeared to me that, during the first half of the metamorphosis, the length rather decreases somewhat than increases, but the individual differences are too numerous to state this phenomenon as certain. I am of opinion, that the fact that the larva does not grow during the metamorphosis, must be attributed to its not taking food during this period. Presently I shall revert to the grounds of this.

Before the metamorphosis both the mouth and the gill-slits lie perfectly asymmetrically; the mouth does not lie medianly and ventrally as with all vertebrates, but on the left-side of the body, and of the gill-slits is only the row of the later left-side extant. They behave very curiously, for they do not originate on the left-side, but apparently in the median plane, whilst the foremost of the

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[1]) Larvas from the neighbourhood of Messina are during the metamorphosis still smaller. According to the statements of the authors their length amounts to an average only to $3^1/_2$ mm.

row soon remove temporarily to the right-side of the larva. They open freely outward and not in a gill-cavity or atrium, which is only formed during the metamorphosis by the fusion of a longitudinal fold, which has formed itself, during the larval growth period, on the left-side of the body over the gill-slits with a similar fold, which has developed itself on the right-side of the body.

During the metamorphosis appears likewise the right row of the gill-slits — 8, rarely 7 or 9, in number — which do not open directly outward but in the gill-cavity. The slits of the left side, which had temporarily removed to the right side, return now to the side to which they belong.

I can confirm WILLEY's observation, that the first left gill-slit aborts, and that also the 10th to the 16th disappear during the metamorphosis. At the end of the metamorphosis the young animal is then symmetrical with regard to the gill-slits, and there are 8 of them on the left-side corresponding with the eight on the right-side. It is of secondary importance that the symmetry is somewhat oblique; every left gill-slit does not lie exactly directly opposite the right one, but half the width of the slit more rostral. A similar oblique symmetry is likewise shown by the nerves and muscles of the body of the left-side compared with those of the right-side of the animal.

With the exception of the foremost slit, which remains undivided, as long as the animal lives, each slit is divided into two parts, in a longitudinal direction, by a clasp or "tongue" growing from the dorsal rim, till it reaches the ventral rim with which it fuses.

Directly after the metamorphosis the animal possesses thus, both on the right and on the left side, a row of 8 (rarely 7 or 9) gill-slits. During the rapid growth that follows now, this number regularly increases during the whole life-time of the animal, because constantly a new pair of slits develop themselves at the hindmost part of the gill-basket.

But after the metamorphosis the mouth 1) seems to be a symmetrical organ; it is no longer situated distinctly on the left-side of the body as in the larval growth-period, but more ventrally and almost halved by the median plane as with all vertebrates.

The symmetrical placing of the *gill-slits* is real; since 1893 I have demonstrated however that the symmetrical placing of the *mouth* of Amphioxus is only so in appearance. In reality the mouth, also of the full-grown Amphioxus, is an organ of the left-side; for its inner parietes are exclusively provided for by nerves of the left-side, and

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1) Not to be mistaken for the mouth of the larva, see the conclusion of this article.

its muscles belong all to those of the left-side. No nerve and no muscle of the right-side takes part in the provision of the mouth-cavity.

Here we are in the presence of a remarkable phenomenon: The mouth of Amphioxus, as organ of the left-side, cannot be homologous with the unpaired mouth of vertebrates always developing symmetrically, and we must surmise that on the right-side of the young larva a similar organ as the mouth, a counterpart of it, is found. This organ is, as I indicated a long time ago already, the so-called club-shaped gland and the mouth together with this gland form morphologically the first pair of gill-slits of the Amphioxus-larva.

Instead of gill-*slits,* it is more correct to speak of gill-pouches, for in all vertebrates, without any exception, a gill-slit is formed, because a pouch-shaped projecting part of the gut reaches the epidermis, fuses with it on that spot, and afterwards splits to the outside. With Amphioxus this is exactly the same; here also is every gill-slit formed as a pouch-shaped projecting part of the gut, and splits afterwards — before the metamorphosis — to the outside, after the beginning of the metamorphosis, towards the gill-cavity (the atrium). The epithelium of a gill-pouch can partly differentiate to glandular-epithelium, in this way e. g. in all vertebrates the thymus if formed, a glandulous organ, from the epithelium of some gill-pouches.

The club-shaped gland possesses all the essential distinctive properties of a gill-pouch; it is formed on the right-side of the body as a projecting part of the gut, which opens afterwards to the outside and possesses then two openings one inside in the pharynx, the other to the outside.

Though the greater part of its epithelium has differentiated into glandular epithelium, I found however laterally from it a ring-shaped strip of ciliated epithelium, corresponding entirely to that of the other gill-pouches.

The outside opening of the club-shaped gland is in the beginning placed near to or in the median plane; afterwards it removes in front of the mouth to the left-side of the body. This is again one of the remarkable phenomena of asymmetry in the larva of Amphioxus, the explanation of which I intend to give in my detailed paper [1]), as it would lead me too far here. The club-shaped gland disappears in the course of the metamorphosis, and does not leave any vestige behind.

Has the mouth of the Amphioxus-larva originally also been a gill-slit? In my opinion there is no doubt about it. It is true that

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[1]) This paper was offered last winter to be published in the transactions of the Academy.

it does not originate as a pouch-shaped projecting part, but this is impossible, because in the place where the mouth of the young larva will open, the pharynx lies already directly against the epidermis. Neither is a ciliated gill-epithelium formed in this place, but one has no right to expect it here, because the function of a mouth is so entirely different from that of a gill-slit. On the other hand the mouth possesses another lasting distinctive property, which is peculiar to every gill-slit during the period of growth, but disappears from these slits in the course of the metamorphosis. I found namely, that each gill-slit of the young larva is accompanied in front and behind by a strong gill-muscle, the fibres of which, for the greater part, run in a transversal direction with regard to the axis of the body. Some fibres however, surround the outside gill-opening and form a sphincter round it.

The mouth-opening is likewise enclosed by two such muscles. They degenerate also, but they are not lost without leaving a trace, as the gill-muscles proper, but produce the lip-muscles and the ring-shaped sphincter of the velum.

Mouth and club-shaped gland are counterparts, for they originate one under the second myotome of the left-side, the other under the second myotome of the right-side of the body.

In vertebrates the first pair of gill-slits originates nearly under the second myotome, of which in the head of Selachians nine are formed, as I demonstrated more than 30 years ago for the genera Scyllium and Pristurius [1]. In Selachians the first gill-slit does not any longer function as such either; in rays it serves to admit instead of to let out the respiration-water, and in some sharks this slit, known by the name of spiracle, is shut by the fusion of its parietes. The mouth of Amphioxus is, according to what has just been seen, homologous with the left spiracle of Selachians, and serves, just as in rays, to ingest the respiration-water, but this water contains here the necessary nutriment for the animal.

If now the mouth of the Amphioxus-larva was originally the first gill-slit, then a primitive mouth, homologous with that of vertebrates, must have been extant before this secondary mouth.

This primitive mouth is, in my opinion, represented by the opening

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[1] Braus pretends that not 9 but at least 11 should be formed. A repeated investigation, which will be published afterwards, has taught me that my number 9 for Scyllium and Pristurius is correct, and may be admitted as the normal one for Selachians. In some genera however vertebrate elements fuse secondarily with the skull.

of the so-called praeoral pit, which is formed as a sejoined part of the pharynx and soon opens to the outside.

In accordance with this view is the place where the thyroid gland of Amphioxus originates. In all vertebrates this gland is formed as a median outgrowth of the epithelium of the pharyna immediately behind the mouth, between the first pair of gill-slits, if they are taken as fused with their ventral extremities. If now we see in the mouth of Amphioxus the homologue of that of vertebrates, then, in an incomprehensible way, the thyroid gland of Amphioxus would be formed in front of the mouth instead of behind it.

What explanation can now be given of the fact, that Amphioxus has lost its primitive mouth and has obtained secondarily the first gill-slit as mouth, whilst in the stage of the larval growth — now letting alone the club-shaped gland — not the gill-slits of the right-side, but only those of the left-side open to the exterior and moreover in the median plane, whilst they even partly remove temporarily to the right-side?

The key to this explanation is, in my opinion, to be found in the movement of the young embryo which has been observed by Hatschek. This embryo moves, turning on its longitudinal axis, helicoidally forward; the rotation takes place from right to left.

If now one admits that ancestors of Amphioxus have moved forward in this way, to which they may have been induced, because they missed an auditive or equilibrium-organ, the trace of which does not even appear in Amphioxus, then it is to be understood that the left first gill-slit must have had the predominance over the medianly placed primitive mouth as opening for the admittance of water, which must serve at the same time both for respiration and for nutrition. The following gill-slits had to evacuate the respiration-water, but this evacuation was for the slits on the left-side impeded by the way of moving of the animal. On account of the rotation from right to left, the following gill-slits on the left-side would be inclined to ingest water instead of evacuating it, and therefore they were obliged to remove from this side to the median plane, or still better to the right-side, where the evacuation of the respiration-water was exactly facilitated in consequence of the movement.

By this removal, however, came the original gill-slits of the right-side in a tight place; they remained little, and this is the reason why in the Amphioxus-larva, they appear only in the period of the metamorphosis.

When later ancestors of Amphioxus gave up their swimming way of living and buried themselves into the sand, as he does still now, to dash forward from it with the quickness of an arrow, when he is disturbed, and then to return immediately again into the sand, the reason for asymmetry did not exist any longer, the gill-basket became symmetrical again, and the mouth also tried to assume a symmetrical position, though it could only apparently succeed in it, as it is an organ of the left-side.

It is not to be wondered at, that there are investigators who oppose these views, because they cannot admit that such an ancestral organ, as the primitive mouth, should have had to give way to a secondary mouth. They admit, that ancestors of Amphioxus, which gave up the swimming way of living, have first passed through a period, in which they lay on the sand in the way of flat-fishes instead of burying themselves into it; that then the mouth has removed to the left side, just as, with flat-fishes, one eye, which otherwise would be directed downward to the bottom of the sea, removes to the upperside.

This theory is untenable especially for three reasons:

1ly. The mouth of the Amphioxus-larva does not originate medianly to remove afterwards to the left-side. It originates on the contrary on the left-side to take afterwards a pseudo-median position.

2ly. There is no reason why a median organ, when removing to the left-side should lose its nerves and muscles of the right-side. Not a vestige of such a phenomenon can e.g. be discovered in the heart and the stomach of man, which are for the greater part situated on the left-side.

3ly. One of the characteristic properties of the second myotome of Selachians is the fact, that its cavity remains, for a long time, in communication with the part of the body-cavity that is situated in the lower jaw and is known by the name of mandibular cavity. This communication continues to exist for a long time after the cavities of the following myotomes have sejoined from the body-cavity.

The same is the case with the larva of Amphioxus, and in order to make out, whether the mouth of this larva corresponds, either with that of vertebrates, or with their foremost left gill-slit, one need only state, whether the mandibular cavity of the Amphioxus-larva is situated before or behind the opening of the mouth.

On the base of investigations of Goldschmidt made on an affined larva, called by him Amphioxides, (and in the beginning supposed to be a developed form) I surmised at the time, that I could solve this dilemma in the sense that really the mouth of Amphioxides lies behind the mandibular cavity. In a later publication Goldschmidt has not contradicted this conclusion, but MAC-BRIDE asserted in 1909 that in the Amphioxus-larva the mandibular cavity should lie behind the mouth. When I had the privilege of receiving a few years ago Amphioxus-larvas from the Zoological stations at Naples and in Helgoland, my attention was specially directed to this point, and I found in all the series of my sections of the larval growth-period, but also in the beginning of the metamorphosis, that the mandibular cavity does not run behind the mouth-opening, as MAC-BRIDE asserts, but before it. In my opinion it has hereby been definitely proved that the mouth-opening of the Amphioxus-larva is homologous with the left spiracle of Selachians.

In the course of the metamorphosis the mandibular cavity develops round the mouth, first in the shape of a horse-shoe and afterwards in the shape of a ring, because the extremities of the horse-shoe unite themselves with each other behind the mouth and form the ring-shaped cavity of the velum. As soon as this cavity has assumed the shape of a ring, one can of course no longer see, whether it was situated originally before or behind the mouth.

Finally I may be allowed to give a short communication of the remarkable variations which the mouth of the larva undergoes, of which we know already from HATSCHEK that it invaginates to the inside und transits into the ring-shaped velum-fold, which, in the full-grown animal, separates the mouth-cavity from the throat (pharynx). This invagination is accompanied, during the metamorphosis, by the formation of a longitudinal fold of the skin, extending along the left side of the mouth of the larva and of the praeoral pit.

Hereby is formed an open cavity before the mouth of the larva: the mouth-cavity of the full-grown animal, in which likewise the praeoral pit is lodged, and which, by a longitudinal slit along which the cirri sprout forth, opens to the outside. This slit is known as the mouth-slit of the developed animal.

At the end of the embryonal period, when the larva is only 1 m.m. long, and the first gill-slit is on the point of opening to the exterior, the mouth is a little almost round opening on the left-side of the body under the second myotome. It lies then opposite the club-shaped gland, which is found under the second myotome of the right-side.

With the growth of the larva the mouth-opening, which is now oval and becomes afterwards slit-shaped, increases giganticly in length. When three gill-slits are extant, the mouth reaches as far to the back as the back-rim of the first slit, and at the end of the larval growth-period it reaches even the back-rim of the fourth or fifth gill-slit. This gigantic enlargement[1]) of the mouth indicates that the larva, during its growth, must be a very gluttonous animal, if the words gigantic and gluttonous may be applied to an animal that is not even 5 m.m. long. The gluttony is also of a very inoffensive nature and consists in swallowing water, for only minimal remnants of food are found in the gut.

During the metamorphosis remarkable modifications occur at the mouth of the larva.

One modification regards its size. In the first half of the period of metamorphosis the gigantic mouth becomes constantly smaller, till, in the middle of this period, it is an extremely little round hole. But for a little sickle-shaped slit this hole is moreover closed by the formation, at the rostral rim, of the first tentacle in the shape of a little tongue.

Now the falling asunder and the resorption of the gill-muscles is in full swing. The fibres of these muscles let loose from their insertions and have partly been broken into pieces. Just like the loosened cells of the club-shaped gland these pieces float in the fluid that is found in the body-cavity.

From this phenomenon, from the cessation of the growth and from the minimal size of the mouth I deduce, that the animal ceases to take food from outside, and continues to live at the expense of part of its own texture: the gill-muscles and the cells of the club-shaped gland.

Obviously the gill-muscles have become superfluous, in consequence of the formation of the atrium, which now regulates for the greater part the movements of respiration. No trace of gill-muscles appears at the slits of the right-side of the body, which never open directly to exterior, but only indirectly by means of the atrium.

In the second half of the metamorphosis the mouth enlarges again gradually, and becomes the opening of the "velum", round which three more tentacles develop, completing the number of four, which this opening is provided with.

The diminution of the mouth has already partly been observed by Legros, but vehemently contested by Willey, who supposes this diminution to be only apparent, an optical effect, caused by the rotation of the mouth on a sagittal axis.

According to Willey, who does not base his views on the study of sections, but only on that of the larva in *toto*, this rotation should commence already at the beginning of the metamorphosis. I found

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[1]) This enlargement of the mouth contributes to the temporary removal of the foremost gill-slits of the left-side to the right-side.

however that this rotation, which is incomprehensibly denied by Legros does not set in before the mouth has reached its minimal size, consequently in the middle of the period of the metamorphosis. In consequence of this rotation the rostral rim of the mouth of the larva becomes right-rim, whilst at the same time the posterior rim becomes left-rim.

The mouth-opening having become velaropening lies now symmetrically with regard to the median plane, but the nerves, that surround it, indicate that it continues to be an organ of the leftside.

In the higher animals the middle-ear originates from the first gill-pouch, whilst amphioxus lacks the auditive organ entirely. If we wish to express ourselves in a popular way, we may say, as I did already on a former opportunity: Amphioxus cannot hear; he eats however with the left ear, and has consequently lost the mouth.

Mathematics. — *"Applications of* Sonine's *extension of* Abel's *integralequation."* By Dr. J. G. Rutgers. (Communicated by Prof. W. Kapteyn).

(Communicated in the meeting of September 27, 1913).

Sonine [1]) has given to Abel's integralequation an extension which comes to the following.

The unknown function u in the equation

$$f(x) = \int_a^x \psi'(x-\xi)\, u(\xi) d\xi \quad \ldots\ldots \quad (1a)$$

is determined by

$$u(x) = \int_a^x \sigma(x-\xi)\, f'(\xi) d\xi \quad \ldots\ldots \quad (2a)$$

where we suppose $f(x)$ to be finite and continuous, $f'(x)$ finite, $a \leq x \leq b$, and $f(a) = 0$. Moreover σ and ψ are connected in the following way:

Suppose

$$\varphi(y) = \sum_0^\infty c_m y_m \quad , \quad \frac{1}{\varphi(y)} = \sum_0^\infty d_n y^n,$$

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[1]) Acta Matem. **4**; 1884.

then if

$$a_m = \frac{c_m}{\Gamma(m-\lambda+1)} \quad , \quad b_n = \frac{d_n}{\Gamma(n+\lambda)}$$

we shall find

$$\psi(x) = x^{-\lambda} \sum_0^\infty a_m x^m \text{ and } \sigma(x) = x^{-(1-\lambda)} \sum_0^\infty b_n x^n,$$

and at the same time we find λ bound to the condition $1 > \lambda > 0$.

This rather intricate connection between ψ and σ greatly limits the number of applications with some practical significance. As a matter of fact Sonine gives two, for the third furnishes nothing new as we shall see.

1. Abel's equation appears when in (1a) we take: $\psi(x) = \frac{1}{x^\lambda}$ $(1 > \lambda > 0)$. By this $a_0 = 1$, $a_m = 0\ (m > 0)$, by which $c_0 = \Gamma(1-\lambda)$, $c_m = 0\ (m > 0)$ and therefore

$$q(y) = \Gamma(1-\lambda) \quad , \quad \frac{1}{q(y)} = \frac{1}{\Gamma(1-\lambda)};$$

furtheron

$$d_0 = \frac{1}{\Gamma(1-\lambda)} \quad , \quad d_n = 0\ (n > 0)$$

and therefore

$$b_0 = \frac{1}{\Gamma(1-\lambda)\,\Gamma(\lambda)} = \frac{\sin \lambda\pi}{\pi} \quad , \quad b_n = 0\ (n > 0).$$

Finally follows:

$$\sigma(x) = \frac{\sin \lambda\pi}{\pi} \cdot \frac{1}{x^{1-\lambda}}.$$

Substitution of ψ and σ in (1a) and (1b) now gives us:

$$f(x) = \int_a^x \frac{u(\xi)}{(x-\xi)^\lambda}\, d\xi \quad , \quad u(x) = \frac{\sin \lambda\pi}{\pi} \int_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}}\, d\xi \quad . \quad . \quad (2)$$

2. For the second application Sonine starts from [1]:

$$q(y) = \Gamma(1-\lambda) e^{-\frac{z^2 y}{4}} = \Gamma(1-\lambda) \sum_0^\infty \frac{(-1)^m \left(\frac{z^2 y}{4}\right)^m}{m!},$$

so that

$$c_m = \Gamma(1-\lambda) \frac{(-1)^m \left(\frac{z^2}{4}\right)^m}{m!}, \text{ thus } a_m = \Gamma(1-\lambda) \cdot \frac{(-1)^m \left(\frac{z}{2}\right)^{2m}}{m!\, \Gamma(m-\lambda+1)}$$

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[1] The factor $\Gamma(1-\lambda)$ is added for practical reasons.

by which

$$\psi(x) = \Gamma(1-\lambda)x^{-\lambda} \sum_0^{\infty} \frac{(-1)^m \left(\frac{z\sqrt{x}}{2}\right)^{2m}}{m!\ \Gamma(m-\lambda+1)} = \Gamma(1-\lambda)\left(\frac{z}{2}\right)^{\lambda} x^{-\frac{\lambda}{2}} I_{-\lambda}(z\sqrt{x})$$

Further we find

$$\frac{1}{\varphi(y)} = \frac{1}{\Gamma(1-\lambda)} e^{\frac{z^2y}{4}} = \frac{1}{\Gamma(1-\lambda)} \sum_0^{\infty} \frac{\left(\frac{z^2y}{4}\right)^n}{n!},$$

so that

$$d_n = \frac{1}{\Gamma(1-\lambda)} \cdot \frac{\left(\frac{z}{2}\right)^{2n}}{n!},$$

thus

$$b_n = \frac{1}{\Gamma(1-\lambda)} \cdot \frac{\left(\frac{z}{2}\right)^{2n}}{n!\ \Gamma(n+\lambda)} = \frac{\sin \lambda\pi\ \Gamma(\lambda)}{\pi} \cdot \frac{\left(\frac{z}{2}\right)^{2n}}{n!\ \Gamma(n+\lambda)},$$

by which

$$\sigma(x) = \frac{\sin \lambda\pi\ \Gamma(\lambda)}{\pi} x^{-(1-\lambda)} \sum_0^{\infty} \frac{\left(\frac{z\sqrt{x}}{2}\right)^{2n}}{n!\Gamma(n+\lambda)} =$$

$$= \frac{i^{1-\lambda} \sin \lambda\pi\ \Gamma(\lambda)}{\pi} \left(\frac{z}{2}\right)^{1-\lambda} x^{-\frac{1-\lambda}{2}} I_{-(1-\lambda)}(iz\sqrt{x}).$$

By substitution of these values of ψ and σ we see that (1*a*) and (1*b*) pass into

$$f(x) = \Gamma(1-\lambda)\left(\frac{z}{2}\right)^{\lambda} \int_a^x (x-\xi)^{-\frac{\lambda}{2}} I_{-\lambda}(z\sqrt{x-\xi})\, u(\xi)\, d\xi \quad . \quad . \quad (3a)$$

with

$$u(x) = \frac{i^{1-\lambda} \sin \lambda\pi\ \Gamma(\lambda)}{\pi}\left(\frac{z}{2}\right)^{1-\lambda} \int_a^x (x-\xi)^{-\frac{1-\lambda}{2}} I_{-(1-\lambda)}(iz\sqrt{x-\xi}) f'(\xi) d\xi . \ (3b)$$

For $\lambda = \frac{1}{2}$ follow from this some important relations as Sonine already noticed. The forms of Abel appear when we take $z = 0$.

3. As third application Sonine gives:

$$\varphi(y) = \Gamma(1-\lambda)(1+zy)^{-(1-\lambda)} = \sum_0^{\infty} (-1)^m \frac{\Gamma(m-\lambda+1)}{m!} (zy)^m,$$

by which

$$c_m = (-1)^m \cdot \frac{\Gamma(m-\lambda+1)}{m!} z^m \quad , \quad a_m = \frac{(-1)^m z^m}{m!},$$

thus

$$\psi(x) = x^{-\lambda} \sum_0^\infty (-1)^m \frac{(zx)^m}{m!} = \frac{e^{-zx}}{x^\lambda}.$$

Further ensues

$$\frac{1}{\varphi(y)} = \frac{1}{\Gamma(1-\lambda)}(1+zy)^{1-\lambda} = \frac{\lambda-1}{\Gamma(1-\lambda)\Gamma(\lambda)} \sum_0^\infty (-1)^n \frac{\Gamma(n+\lambda-1)}{n!}(zy)^n,$$

so that

$$d_n = \frac{(\lambda-1)\sin\lambda\pi}{\pi} \cdot \frac{(-1)^n \, \Gamma(n+\lambda-1)}{n!} z^n \, , \; b_n = \frac{(\lambda-1)\sin\lambda\pi}{\pi} \, \frac{(-1)^n z^n}{n!(n+\lambda-1)}$$

and therefore

$$\sigma(x) = \frac{(\lambda-1)\sin\lambda\pi}{\pi} x^{\lambda-1} \sum_0^\infty \frac{(-1)^n (zx)^n}{n!(n+\lambda-1)},$$

to which SONINE gives another form, which is, however, not correct. It would be better to write for it:

$$\sigma(x) = \frac{\sin\lambda\pi}{\pi}\left[\frac{1}{x^{1-\lambda}} - (1-\lambda)\sum_1^\infty (-1)^n \frac{z^n x^{n+\lambda-1}}{n!\,(n+\lambda-1)}\right],$$

for indeed it is now again evident that for $z=0$ we find ψ and σ assuming the form as in § 1.

Substitution of ψ and σ in (1*a*) and (1*b*) (SONINE leaves this out) now gives:

$$f(x) = \int_a^x \frac{e^{-z(x-\xi)}}{(x-\xi)^\lambda} u(\xi)\, d\xi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

with

$$u(x) = \frac{\sin\lambda\pi}{\pi}\int_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}} d\xi - \frac{(1-\lambda)\sin\lambda\pi}{\pi}\int_a^x f'(\xi)\left\{\sum_1^\infty \frac{(-1)^n z^n (x-\xi)^{n+\lambda-1}}{n!\,(n+\lambda-1)}\right\} d\xi.$$

As $1 > \lambda > 0$ and $f(a) = 0$, we find that by means of partial integration the last integral passes into:

$$\int_a^x f(\xi)\left\{\sum_1^\infty (-1)^n \frac{z^n (x-\xi)^{n+\lambda-2}}{n!}\right\} d\xi,$$

so that

$$u(x) = \frac{\sin\lambda\pi}{\pi}\int_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}} d\xi - \frac{(1-\lambda)\sin\lambda\pi}{\pi}\int_a^x \frac{e^{-z(x-\xi)}-1}{(x-\xi)^{2-\lambda}} f(\xi)\, d\xi \quad . \quad (4b)$$

That (4*a*) and (4*b*) do not stand for anything new, we shall immediately see by substituting

$$f(x) = e^{-zx} f_1(x) \quad \text{and} \quad u(x) = e^{-zx} u_1(x) \, ,$$

where (4*a*) takes at once the form of ABEL's equation and (4*b*) as its solution can easily be reduced to its ordinary form.

In the following paragraphs we shall be led to really new applications.

4. Let in the first place

$$\varphi(y) = \Gamma(1-\lambda)\,(1+z^2y^2)^{-\frac{1-\lambda}{2}} = \frac{\Gamma(1-\lambda)}{\Gamma\left(\frac{1-\lambda}{2}\right)} \sum_0^\infty (-1)^m \frac{\Gamma\left(m+\frac{1-\lambda}{2}\right)}{m!} (zy)^{2m},$$

where, by application of

$$\Gamma(\alpha)\;\Gamma(\alpha+\tfrac{1}{2}) = \frac{\sqrt{\pi}}{2^{2\alpha-1}} \cdot \Gamma(2\alpha) \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

we find that

$$c_{2m} = \frac{\Gamma\left(1-\frac{\lambda}{2}\right)}{2^\lambda \sqrt{\pi}} \cdot (-1)^m \frac{\Gamma\left(m+\frac{1-\lambda}{2}\right)}{m\,!} z^{2m}, \quad c_{2m+1} = 0$$

and thus, again because of (5):

$$a_{2m} = \frac{\Gamma\left(1-\frac{\lambda}{2}\right)}{2^\lambda \sqrt{\pi}} \cdot (-1)^m \frac{\Gamma\left(m+\frac{1-\lambda}{2}\right)}{m!\,\Gamma(2m-\lambda+1)} z^{2m} =$$

$$= \Gamma\left(1-\frac{\lambda}{2}\right) \cdot (-1)^m \frac{\left(\frac{z}{2}\right)^{2m}}{m!\,\Gamma\left(m-\frac{\lambda}{2}+1\right)} \, , \quad a_{2m+1} = 0 \, ,$$

so that:

$$\psi(x) = x^{-\lambda}\, \Gamma\left(1-\frac{\lambda}{2}\right) \sum_0^\infty \frac{(-1)^m \left(\frac{zx}{2}\right)^{2m}}{m!\,\Gamma\left(m-\frac{\lambda}{2}+1\right)} = \Gamma\left(1-\frac{\lambda}{2}\right) \left(\frac{z}{2x}\right)^{\frac{\lambda}{2}} I_{-\frac{\lambda}{2}}(zx)$$

Furthermore we find

$$\frac{1}{\varphi(y)} = \frac{1}{\Gamma(1-\lambda)} \cdot (1+z^2y^2)^{\frac{1-\lambda}{2}} = \frac{1}{\Gamma(1-\lambda)\,\Gamma\left(\frac{\lambda-1}{2}\right)} \cdot \sum_0^\infty (-1)^n \frac{\Gamma\left(n-\frac{1-\lambda}{2}\right)}{n\,!} (zy)^{2n} \, ,$$

by which, on account of (5):

$$d_{2n} = \frac{(\lambda-1)\,\Gamma\left(\frac{\lambda}{2}\right)}{2^{2-\lambda}\sqrt{\pi}} \cdot \frac{\sin \lambda\pi}{\pi} \cdot (-1)^n \frac{\Gamma\left(n - \frac{1-\lambda}{2}\right)}{n\,!} z^{2n} \;,\; d_{2n+1} = 0$$

and thus, again on account of (5):

$$b_{2n} = \frac{(\lambda-1)\,\Gamma\left(\frac{\lambda}{2}\right)}{2^{2-\lambda}\sqrt{\pi}} \; \frac{\sin \lambda\pi}{\pi} \cdot (-1)^n \frac{\Gamma\left(n - \frac{1-\lambda}{2}\right)}{n!\,\Gamma(2n+\lambda)} z^{2n} =$$

$$= (\lambda-1)\,\Gamma\left(\frac{\lambda}{2}\right) \frac{\sin \lambda\pi}{\pi} \cdot (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n!\,\Gamma\left(n+\frac{\lambda}{2}\right)(2n+\lambda-1)} \;,\; b_{2n+1} = 0,$$

so that

$$\sigma(x) = (\lambda-1)\;\Gamma\left(\frac{\lambda}{2}\right) \frac{\sin \lambda\pi}{\pi} \sum_0^\infty (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n!\,\Gamma\left(n+\frac{\lambda}{2}\right)} \cdot \frac{x^{2n+\lambda-1}}{2n+\lambda-1} =$$

$$= \frac{\sin \lambda\pi}{\pi} \cdot \frac{1}{x^{1-\lambda}} - (1-\lambda)\;\Gamma\left(\frac{\lambda}{2}\right) \frac{\sin \lambda\pi}{\pi} \sum_1^\infty (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n!\;\Gamma\left(n+\frac{\lambda}{2}\right)} \frac{x^{2n+\lambda-1}}{2n+\lambda-1}.$$

For $z = 0$ we are evidently again in the special case of ABEL's problem (§ 1).

Let us now substitute ψ and σ now found in (1*a*) and (1*b*), we then arrive at the integralequation

$$f(x) = \Gamma\left(1-\frac{\lambda}{2}\right)\left(\frac{z}{2}\right)^{\frac{\lambda}{2}} \int_a^x (x-\xi)^{-\frac{\lambda}{2}}\, I_{-\frac{\lambda}{2}}\{z(x-\xi)\}\, u(\xi)\, d\xi, \qquad (6a)$$

to which belongs as solution:

$$u(x) = \frac{\sin \lambda\pi}{\pi} \int_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}}\, d\xi -$$

$$- \frac{\sin \lambda\pi\,(1-\lambda)\;\Gamma\left(\frac{\lambda}{2}\right)}{\pi} \int_a^x f'(\xi)\, d\xi \left\{ \sum_1^\infty (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n!\;\Gamma\left(n+\frac{\lambda}{2}\right)} \cdot \frac{(x-\xi)^{2n+\lambda-1}}{2n+\lambda-1} \right\}$$

As $1 > \lambda > 0$, $f(a) = 0$ and $f(x)$ is finite the last integral passes by means of partial integration into

$$\int\limits_a^x f(\xi)\,d\xi \left\{ \sum_1^\infty (-1)^n \frac{\left(\frac{z}{2}\right)^{2n} (x-\xi)^{2n+\lambda-2}}{n!\,\Gamma\left(n+\frac{\lambda}{2}\right)} \right\},$$

so that we find

$$\left.\begin{aligned} u(x) = \frac{\sin\lambda\pi}{\pi}\int\limits_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}}\,d\xi \, - \\ -\frac{\sin\lambda\pi\,(1-\lambda)}{\pi}\int\limits_a^x \left[\Gamma\left(\frac{\lambda}{2}\right)\left(\frac{z}{2}\right)^{1-\frac{\lambda}{2}} I_{-\left(1-\frac{\lambda}{2}\right)}\{z\,(x-\xi)\} - \frac{1}{(x-\xi)^{2-\lambda}}\right] f(\xi)\,d\xi \end{aligned}\right\} \quad (6b)$$

5. In a similar way we find by starting from

$$\varphi(y) = \Gamma(1-\lambda)\,(1+z^2y^2)^{-1+\frac{\lambda}{2}} = \frac{\Gamma(1-\lambda)}{\Gamma\left(1-\frac{\lambda}{2}\right)} \sum_0^\infty (-1)^m \frac{\Gamma\left(m+1-\frac{\lambda}{2}\right)}{m!}\,(zy)^{2m}$$

and

$$\frac{1}{\varphi(y)} = \frac{1}{\Gamma(1-\lambda)}\,(1+z^2y^2)^{1+\frac{\lambda}{2}} = \frac{1}{\Gamma(1-\lambda)\,\Gamma\left(\frac{\lambda}{2}-1\right)} \sum_0^\infty (-1)^n \frac{\Gamma\left(n+\frac{\lambda}{2}-1\right)}{n!}\,(zy)^{2n}$$

successively

$$\psi(x) = \Gamma\left(\frac{1-\lambda}{2}\right)\frac{z}{2}\cdot\left(\frac{2x}{z}\right)^{\frac{1-\lambda}{2}} I_{-\frac{1+\lambda}{2}}(zx),$$

$$\sigma(x) = \frac{\sin\lambda\pi}{\pi}\cdot\frac{1}{x^{1-\lambda}} - (2-\lambda)\,\Gamma\left(\frac{\lambda+1}{2}\right)\frac{\sin\lambda\pi}{\pi}\sum_1^\infty (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n!\,\Gamma\left(n+\frac{\lambda+1}{2}\right)}\cdot\frac{x^{2n+\lambda-1}}{2n+\lambda-2}$$

We can again notice here that for $z=0$ the special forms appear as with Abel's problem.

Substitution in (1*a*) and (1*b*) furnishes the integralequation

$$f(x) = \Gamma\left(\frac{1-\lambda}{2}\right)\left(\frac{z}{2}\right)^{\frac{1+\lambda}{2}} \int\limits_a^x (x-\xi)^{\frac{1-\lambda}{2}} I_{-\frac{1+\lambda}{2}}\{z\,(x-\xi)\}\,u(\xi)\,d\xi, \quad (7a)$$

with its solution;

$$u(x) = \frac{\sin \lambda\pi}{\pi} \int_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}}\, d\xi \; -$$

$$- \frac{\sin \lambda\pi\,(2-\lambda)}{\pi}\, \Gamma\left(\frac{\lambda+1}{2}\right) \int_a^x f'(\xi) d\xi \,.\, \left\{ \sum_1^{\infty} (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n!\,\Gamma\left(n+\frac{\lambda+1}{2}\right)} \cdot \frac{(x-\xi)^{2n+\lambda-1}}{2n+\lambda-2} \right\},$$

of which the last integral can be brought by partial integrating into the form:

$$\int_a^x f(\xi)\, d\xi \,.\, \left\{ \sum_1^{\infty} (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n\,!\;\Gamma\left((n+\frac{\lambda+1}{2}\right)} \cdot \frac{(2n+\lambda-1)(x-\xi)^{2n+\lambda-2}}{2n+\lambda-2} \right\} =$$

$$= \int_a^x f(\xi)\, d\xi \,.\, \left\{ \sum_1^{\infty} (-1)^n \frac{\left(\frac{z}{2}\right)^{2n} (x-\xi)^{2n+\lambda-2}}{n\,!\;\Gamma\left(n+\frac{\lambda+1}{2}\right)} \right\} +$$

$$+ \int_a^x f(\xi)\, d\xi \,.\, \left\{ \sum_1^{\infty} (-1)^n \frac{\left(\frac{z}{2}\right)^{2n}}{n\,!\;\Gamma\left(n+\frac{\lambda+1}{2}\right)} \cdot \frac{(x-\xi)^{2n+\lambda-2}}{2n+\lambda-2} \right\};$$

by partial integrating the last part we find for it, if we put: $f^{(-1)}(x) = \int f(\xi)\, d\xi$:

$$\int_a^x f^{(-1)}(\xi)\, d\xi \,.\, \left\{ \sum_1^{\infty} (-1)^n \frac{\left(\frac{z}{2}\right)^{2n} (x-\xi)^{2n+\lambda\;\;3}}{n\,!\;\Gamma\left(n+\frac{\lambda+1}{2}\right)} \right\}.$$

Summarizing we arrive at the following form for the solution of (7*a*):

$$\left.\begin{aligned} u(x) = {} & \frac{\sin \lambda\,\pi}{\pi} \int_a^x \frac{f'(\xi)}{(x-\xi)^{1-\lambda}}\, d\xi \; - \\ & - \frac{\sin \lambda\,\pi\,(2-\lambda)}{\pi} \int_a^x \left[\Gamma\left(\frac{\lambda+1}{2}\right) \left(\frac{z}{2}\right)^{\frac{1-\lambda}{2}} (x-\xi)^{-\frac{3-\lambda}{2}} I_{-\frac{1-\lambda}{2}} \{z(x-\xi)\} \; - \right. \\ & \qquad \left. - \frac{1}{(x-\xi)^{2-\lambda}} \right] \left\{ f(\xi) + \frac{f^{(-1)}(\xi)}{x-\xi} \right\} d\xi \end{aligned}\right\} (7b)$$

Physics. — *"A mechanical theorem of* BOLTZMANN *and its relation to the theory of energy quanta".* By Prof. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of November 29, 1913).

When black or also not black radiation is compressed reversibly and adiabatically by compression of a perfectly reflecting enclosure, it is known that the following takes place: The frequency ν_p and the energy E_p of each of the principal modes of vibration of the cavity increase during the compression in such a way that we get:

$$\delta\left(\frac{E_p}{\nu_p}\right)=0 \qquad (p=1,2,\ldots,\infty) \quad \ldots\ldots \quad (1)$$

for each of the infinitely many principal vibrations.

Relation (1) is of fundamental importance for the purely *thermodynamic* derivation of WIEN's law; it is no less so for every statistic theory of radiation, which is to remain in keeping with the second law of thermodynamics[1]. In particular it is also the basis of PLANCK's assumption of differences of energy:[2]

$$\frac{\varepsilon}{\nu}=0, h, 2h, \ldots \quad \ldots\ldots\ldots \quad (2)$$

Of late PLANCK's supposition (2) of the original region (Content of energy of systems vibrating sinusoidally) has been applied to a rapidly extending region. Of course tentatively. Two questions arise:

1. Does there continue to exist an adiabatic relation analogous to equation (1) in the transition of systems vibrating sinusoidally (in which the motion is governed by linear differential equations with constant coefficients) to general systems?

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[1] P. EHRENFEST. Welche Züge der Lichtquantenhypothese spielen in der Theorie der Wärmestrahlung eine wesentliche Rolle? Ann. d. Phys. **36** (1911) p. 91; § 5.

[2] By way of elucidation: differences of energy e. g. of the form

$$\frac{\varepsilon}{\nu^2}=0, h, 2h, \ldots$$

would lead to a conflict with the second law of thermodynamics. It is known that PLANCK arrived at (2) by first carrying out his combinatory calculation in general on the assumption

$$\varepsilon=0 \;,\; f(\nu) \;,\; 2f(\nu) \;,\; 3f(\nu), \ldots$$

and by then determining the form of $f(\nu)$ from the condition that the formula of radiation found by the combinatory way shall satisfy WIEN's law. Thus he brought his energy quanta *implicite* in harmony both with relation (1) and with the second law of thermodynamics.

2. If so — how can it be applied heuristically, when Planck's assumption (2) is extended to systems vibrating not sinusoidally?

The answer to the first question is in the affirmative. In the search for the extension of the adiabatic relation (1) I perceived that such an extension, and indeed a surprisingly far-reaching one, follows immediately from a mechanic theorem found by Boltzmann and Clausius independently of each other (see § 1).

For the present I can only answer the second question by giving an example (§ 3). The difficulties which in general present themselves in this — Prof. Einstein drew my attention to the most troublesome one (§ 4) in a conversation — I have stated in § ?, 3, 4, without being able to remove them.

Another objection may be raised against the whole viz.: there is no sense — it may be argued — in combining a thesis, which is derived on the premise of the mechanical equations with the anti-mechanical hypothesis of energy quanta. Answer: Wien's law holds out the hope to us that results which may be derived from classical mechanics and electrodynamics by the consideration of macroscopic-adiabatic processes, will continue to be valid in the future mechanics of energy quanta.

§ 1. Let $q_1, \ldots, q_n$ be the coordinates of a mechanic system. The potential energy Φ may depend, besides on the coordinates q, also on some "slowly variable parameters" $r_1, r_2, \ldots$ Let the kinetic energy T of the system be an homogeneous, quadratic function of the velocities q_1, and contain in its coefficients besides the q's, eventually also the r's.

Let further the system possess the following properties: For definite but arbitrarily chosen values of the parameters $r_1, r_2, \ldots$ all the motions of the system are *periodical,* no matter with what initial phase $(q_1, \ldots, q_n, p_1, \ldots, p_n)$ the system begins. The period P will in general not only depend on the values of $r_1, r_2, \ldots$, but also on the phase (q_0, p_0), with which the system begins.

By changing the parameters $r_1, r_2, \ldots$ infinitely slowly we can transform every original motion (A) of the system into another (B). This particular mode of influencing the system is called "adiabatic influencing" of the motion.

If moreover the respective *periods* of the motion are indicated by P_A and P_B, or their reciprocal values (the "*frequencies*") by ν_A and ν_B, and further the *temporal mean of the kinetic energy* by $\overline{T}_A$ and $\overline{T}_B$, then

$$\left(\frac{\overline{T}}{\nu}\right)_A = \left(\frac{\overline{T}}{\nu}\right)_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

With adiabatic influencing of a periodic system the quotient of the temporal mean of the kinetic energy and of the frequency remains unchanged (adiabatic relation).

If δ' denotes an infinitesimal adiabatic change, P the original period, then:

$$\delta' \left(\frac{\overline{T}}{\nu}\right) = \delta' \int_0^P dt \, . \, T = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

(The action calculated over a period remains constant on adiabatic influencing). The last assertion is nothing but a *special case* of the thesis of BOLTZMANN, CLAUSIUS and SZILY, the derivation and formulation of which may be found in BOLTZMANN's "Vorlesungen über Mechanik", Vol. II, § 48. [1])

§ 2. *Remarks.*

a. In the case that there is no potential energy at all in the system, or that the potential energy is in a fixed ratio to the kinetic energy [2]), the relation

$$\delta' \left(\frac{E}{\nu}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II')$$

holds at the same time as equation (II) (compare equation (1) for systems vibrating sinusoidally). But it is noteworthy that (II') only holds in such particular cases, and is not of such general application as (II).

b. A practical extension of thesis (I) to *non*-periodical motions would be very desirable. That it is not at once possible, follows immediately from early investigations by BOLTZMANN[3]). I prefer not to follow the way which BOLTZMANN chose to extend his thesis to non-periodical systems [4]), because it essentially rests on the untenable [5]) hypothesis of ergodes.

c. In case the adiabatic influencing leads to some singular motions, in which a periodic motion begins to detach itself into two or more separate motions, assertion (II) must be modified accordingly.

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[1]) Original papers: L. BOLTZMANN, Wissensch. Abh. I. p. 23, p. 229. R. CLAUSIUS, Pogg. Ann. **142** p. 433. SZILY, Pogg. Ann. **145**.

[2]) $\overline{\Phi} = \overline{T}$ for systems vibrating sinusoidally, when the potential energy in the state of equilibrium is taken zero.

[3]) L. BOLTZMANN, Ges. Abh. II p. 126 (1877); Vorles. üb. Mechanik II § 41.

[4]) Ges. Abh. III p. 132, 139, 153.

[5]) P. u. T. EHRENFEST Mathem. Encykl. IV. 32 § 10a (ROSENTHAL, Ann. d. Phys. **42** (1913) p. 796; M. PLANCHEREL, Ann. d. Phys. (1913) **42** p. 1061.

Example[1]). Let a point move to and fro free from forces in a tube closed on either side. Let a repulsive field of force arise and increase infinitely slowly in the middle of the tube. At last a moment comes when the point with its store of kinetic energy cannot get any longer through that "wall", and only moves to and fro in one half of the tube. If this field of force is of infinitely small extension, the kinetic energy of the motion is the same at the end as at the beginning; the frequency on the other hand is twice the value, for the path has been halved. Accordingly the original motion has split up into two distinct separated branches during the adiabatic influencing.

§ 3. An example may illustrate the way in which the "adiabatic relation" I may be applied. This example refers to the extension of PLANCK's assumption (5) from resonators vibrating sinusoidally to rotating dipoles.

A fixed dipole may be suspended so that it can revolve freely round the z-axis. Parallel to the x-axis a very strong directional field is made to act. We first consider infinitely small oscillations of the dipole. The angle of rotation may be denoted by q, the corresponding moment (moment of inertia × angular velocity) by p, the frequency of the oscillation by ν_0. According to PLANCK's assumption (2) the image point (q, p) of such a dipole can lie nowhere else in the (q, p)-plane than on certain ellipses, which belong to the quantities of energy $0, h\nu_0$, $2h\nu_0, \ldots$ and for which therefore:

$$\left(\frac{\overline{T}}{\nu}\right)_0 = 0, \quad \frac{h}{2}, \quad 2\frac{h}{2}, \ldots\ldots n\frac{h}{2}, \ldots\ldots \quad (3)$$

We have namely (sinus vibration !):

$$\overline{T} = \frac{\varepsilon}{2} \ldots \quad (4)$$

The infinite number of points of rest and equilibrium:

$$p = 0 \qquad q = 0, \quad \pm 2\pi, \quad \pm 4\pi, \quad \pm 6\pi, \ldots$$

belong to the value of the energy $\varepsilon = 0$.

Some congruent ellipses, which have these points (5) as centres, belong to the value $\varepsilon = nh\nu_0$.

We now consider an adiabatic influencing of such an initial motion of the dipole by an infinitely slow change of the orientating field of force, and eventually also of the moment of inertia. In this way it is possible to convert the infinitely small oscillations into

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[1]) Mr. K. HERZFELD gave this example on the occasion of a discussion.

oscillations of finite amplitude, till at last the dipole changes its form of motion and begins to rotate to the right or to the left; at first still noticeably irregularly, at last with constant velocity of rotation. When we consult Fig. 1, the continuous change of the motion will become clear, particularly also the transition through the singular motion *GH*. A complete oscillation corresponds in the final state to a *double* rotation of the uniformly rotating dipole $(0 \leq q \leq 4\pi)$: *ABE*. Hence if we wish to derive the kinetic energy T_1 of the uniform rotation by the aid of the "adiabatic relation" from the mean kinetic energy T_0 of the original oscillatory motion, we must take as corresponding period the time

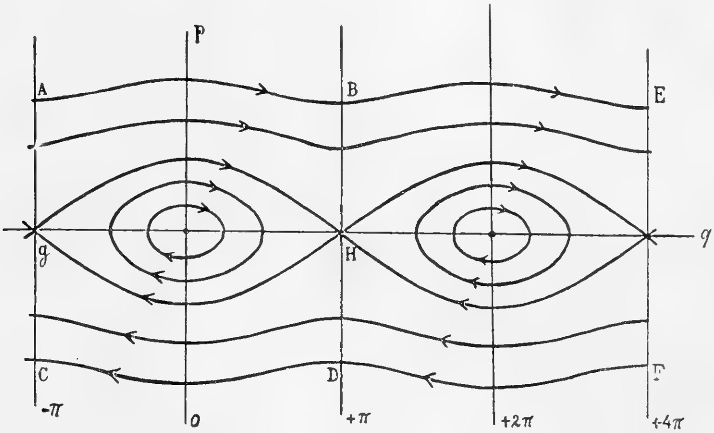

Fig. 1.

$$P_1 = \frac{4\pi}{\dot q_1} \quad \ldots\ldots\ldots\ldots \quad (6)$$

where $\dot q_1$ is the constant velocity of rotation of the dipole; so as corresponding frequency

$$\nu_1 = \frac{\dot q_1}{4\pi} \quad \ldots\ldots\ldots\ldots \quad (7)$$

Then according to (7) (I) and (3), we have

$$\left(\frac{\overline{T}}{\nu}\right)_1 = \frac{4\pi T_1}{\dot q_1} = \left(\frac{\overline{T}}{\nu}\right)_0 = 0\ ,\ \frac{h}{2}\ ,\ 2\frac{h}{2}\ ,\ \ldots\ n\frac{h}{2}\ ,\ \ldots \quad (8)$$

or also, as

$$T_1 = \frac{p_1 q_1}{2} \quad \ldots\ldots\ldots\ldots \quad (9)$$

$$p_1 = 0\ ,\ \pm \frac{h}{4\pi}\ ,\ \pm 2\frac{h}{4\pi}\ ,\ \ldots . \pm n\frac{h}{4\pi}\ ,\ \ldots . \quad (10)^{1)}$$

If other values of p were admitted for a uniformly rotating dipole, it would be possible that by reversal of the described adiabatic process sinusoidal vibrations were obtained, with an amount of energy which would come in collision with PLANCK'S *assumptions* (3) *and* (2).

If we have N dipoles, and if with given total energy, we wish to calculate the "most probable" distribution of the dipoles over the possible motions (10), it is still to be fixed by definition to what regions in the (q,p)-plane the same probability must be assigned. By the "adiabatic influencing" every separate ellipse of PLANCK'S in the (q, p)-plane passes finally into a definite pair of straight lines of the length of 2π, which lie symmetrically on either side of the q-axis. If in the statistic treatment of dipoles vibrating sinusoidally with PLANCK we consider all the separate ellipses as regions of equal probability, we are naturally led to treat the just-mentioned pairs of lines for the uniformly rotating dipoles as regions of equal probability [2]) (Hypothesis A). However natural this may be, yet it is a new hypothesis. Is this hypothesis inevitable?

Seemingly the following course is open. Let us start from N dipoles vibrating sinusoidally (frequency ν_0), which are distributed over PLANCK'S ellipses in the *most probable* manner. Apply the above-described "adiabatic influencing" to all the poles at the same time. Then an entirely definite distribution of the N-dipoles over the different modes of motion is obtained finally (10). This distribution (distribution B) is, however, *another* than follows as the most "probable" from the hypothesis A (distribution A). Is distribution B to be taken as the distribution which corresponds with the state of equilibruim, and is therefore the distribution A and the hypothesis A to be rejected? The remarks made in the following § try to demonstrate that the distribution B *cannot* be considered as a distribution of equilibrium.

§ 4. In case of adiabatic compression black radiation is trans-

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1) In my monograph: "Bemerk. betreffs der specif. Wärme zweiatomiger Gase", Verh. d. deutsch. phys. Ges. **15** (1913) p. 453, I have erroneously put:

$$\nu_1 = \frac{\dot{q}_1}{2\pi} \qquad \text{so} \qquad p_1 = \ldots . \pm n\frac{h}{2\pi} \ldots .$$

This, however, has no further influence on the derivations given there than that the numerical value of the moment of inertia L of the hydrogen molecule calculated finally must be divided by four.

2) P. EHRENFEST. Bemerk. betreffs der specif. Wärme zweiatomiger Gase. Verh. d. deutschen phys. Ges. **15** (1913) p. 453.

formed into black radiation as well when there is a "black grain" in the contracting reflecting enclosure, as in the absence of such a "catalyser". Else we should get into collision with the second law of thermodynamics.[1] If there are N monatomic molecules in a vessel with rough walls, distributed according to MAXWELL's law, and if this ideal gas is compressed by an infinitely slow shifting of the walls of the vessel, the distribution finally follows again MAXWELL's law, both when the molecules during the compression can collide, and when they could penetrate perfectly through each other. Probably more examples might be found in which through an "adiabatic influencing" of the separate degrees of freedom a state of equilibrium arises from a state of equilibrium.[2] But in general this is not the case, e.g. for molecules consisting of more than one atom or for mon-atomic molecules on which an external field of force acts.[3]

Chemistry. — *"Equilibria in ternary systems. XI."* By Prof. F. A. H. SCHREINEMAKERS.

In all our previous communications we have always contemplated the case that the occurring solid substances are ternary compounds. Now we shall assume that a binary compound occurs.

It is evident that we may deduce the saturationcurves under their own vapour-pressure and the boilingpointcurves of a binary compound in the same way as has been done in the previous communications for a ternary compound.

We take a compound composed of B and C, we represent this in fig. 1 by the point F on the side BC of the components-triangle ABC. We now take a definite temperature T and a pressure P in such a way, that no vapour can be formed and the isotherm consists only of the saturationcurve of F. This is represented in fig. 1 by curve pq.

On decrease of P, a gasregion occurs somewhere and also the region $L-G$, which separates gas- and liquidregion from each other.

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[1] M. PLANCK, Wärmtestrahlung II. Aufl. § 71.

[2] The two mentioned cases have this in common that the pressure only depends on the total energy of the system, and not on its distribution over the different degrees of freedom.

[3] In an analogous way we can see that a canonical ensemble of gases generally does *not* remain canonical after an "adiabatic influencing".

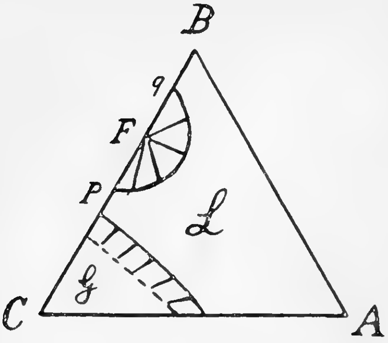

Fig. 1.

These regions may arise either anywhere within the triangle, or on one of the sides or in one of the angular-points; in fig. 1 we may think them arisen in the angular-point C. Also two or more of these regions may be formed in different points of the triangle and they may come together later in different ways.

We will distinguish now three principal cases according to the phenomena in the binary system BC.

I. The equilibrium liquid-gas of the binary system BC shows neither a maximum- nor a minimumpoint of pressure. The pressure of every liquid consisting of B and C is situated, therefore, between the pressure of the pure substances B and C.

II and III. The equilibrium liquid-gas of the binary system BC shows a maximum- or a minimumpoint of pressure.

We take at first the case mentioned sub I; we assume, for fixing the ideas, that the pressure decreases from C to B. The result of this is that every heterogeneous region $L—G$, at every temperature and under every pressure, intersects only once the side BC (fig. 1) and that this region on decrease of P with its liquid-line ahead moves along BC from C to B. Of course it is indifferent, where the gasregion and the region $L—G$ arise, on condition that this does not occur in a point of the side BC (excepted in C itself). Decreasing the pressure, a pressure P_M, occurs, under which the liquidcurve of the region LG and the saturationcurve of F obtain at first a common point; we shall call this point M. P_M, therefore, is the highest pressure, under which the system $F + L + G$ occurs.

When M is situated within the triangle, then, as was formerly deduced, M is a point of contact of the two curves and F, M and the corresponding vapourpoint M_1 are situated on a straight line. The point M then is a point of maximum pressure of the saturationcurve under its own vapourpressure.

When M is situated on the side BC of the triangle, e.g. in the point p of figure 1, the points F, p, and the corresponding vapourpoint on the side BC are, therefore, also situated on a straight line; then usually the two curves do not come in contact with one another. If we imagine in fig. 1 the liquidcurve drawn through p, the two curves will come in contact with one another in p only exceptionally. The pressure P_p is then the highest pressure under which the system

$F + L + G$ occurs, but the point p is not a point of maximum pressure of the saturationcurve under its own vapourpressure (we will refer to this later).

On further decrease of pressure one or more points of intersection are found, therefore also one or more threephasetriangles; the different diagrams may be easily deduced in the same way as in communication I.

On further decrease of pressure we attain a pressure P_m under which the contemplated curves have for the last time a common point; we call this point m. P_m therefore is the lowest pressure under which the system $F + L + G$ can still occur and the points F, m and the corresponding vapourpoint m_1 are situated again on a straight line. When m is situated within the triangle, it is again a point of contact and also a point of minimum pressure of the saturationcurve under its own vapourpressure. When m is situated on the side BC of the triangle, (we imagine in fig. 1 the liquid curve of the region LG through the point q) the two curves do not come in contact with one another in q, and q is not a point of minimum pressure of the saturation curve under its own vapourpressure. Of course P_q is the lowest pressure under which the system $F + L + G$ may yet occur.

Now we will deduce some saturationcurves under their own vapourpressure.

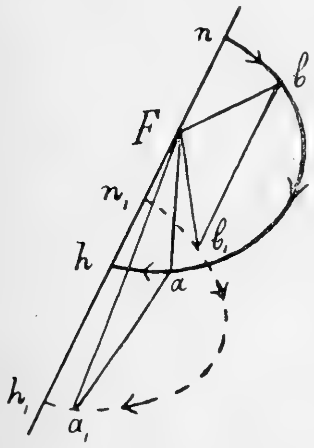

Fig. 2.

$T < T_K$. At first we choose a temperature T lower than the point of maximum sublimation T_K of the binary compound F. In a similar way as we have deduced fig. 11 (I) for the general case, we now find a diagram as is drawn in fig. 2. In this figure however only a part of the componenttriangle ABC is drawn; the line h_1Fn is a part of the side BC. Curve $habn$ is the saturationcurve under its own vapourpressure, $h_1a_1b_1n_1$ the corresponding vapourcurve; we shall call also here both the curves circumphased.

At the deduction of this diagram we have assumed, that on these curves neither a point of maximum- nor a point of minimum pressure occurs; the pressure increases from n to h, without being however in n a minimum and in h a maximum. From the deduction it follows also that the sides solid-liquid and solid-gas of the threephasetriangles must have a position with respect to one another as is drawn in the triangles Faa_1 and Fbb_1.

Formerly (communication V and VI) we have deduced several rules for the movement of the sides of a threephasetriangle on change of pressure. When a saturationcurve under its own vapourpressure and its corresponding vapourcurve are removed comparatively far from the point F, the formation of vapour from $F + L$ takes place on increase of volume and the formation of liquid from $F + G$ on decrease of volume. The threephasetriangle turns on increase of pressure in such a way that the conjugationline solid-vapour goes ahead; on decrease of pressure it turns in opposite direction. If in fig. 2 we make triangle Faa_1 or Fbb_1 turn towards higher or lower pressures, we see that these movements are in accordance with the previous rules.

Also we may imagine on curve $habn$ a point of maximum pressure M and on curve $h_1a_1b_1n_1$ the corresponding point M_1; the points F, M and M_1 are then situated on a straight line. The pressure then increases from h and n towards M. Triangle Faa_1 must then also have another position as is drawn in fig. 2; the line Fa must viz. be situated closer to the side Fh_1 than the line Fa_1. Therefore, when we take two threephasetriangles, situated on different sides of the line FMM_1, they turn their sides solid—gas towards each other. We see that this is also in accordance with our previous considerations.

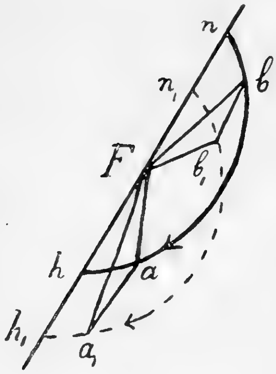

Fig. 3.

We may also imagine a point of minimum pressure m on curve $habn$ and the corresponding point m_1 on curve $h_1a_1b_1n_1$. Triangle Fbb_1 must then have another position; the line Fb_1 must then be situated closer to the side Fn than the line Fb.

$T_K < T < T_F$. We now take a temperature T higher than the point of maximum sublimation T_K, but lower than the minimum-meltingpoint T_F of the substance F. In a similar way as we have deduced for the general case fig. 7 (I), we now find a diagram as fig. 3. Curve $habn$ is circumphased, curve $h_1a_1b_1n_1$ exphased. Further, it is assumed again that on these curves neither a point of maximum- nor a point of minimum pressure occurs. Because the points a and a_1 are removed comparatively far from the point F, the above mentioned rule applies again to the moving of triangle Faa_1 on change of pressure; we see that its turning is in accordance with this rule.

It is different with triangle Fbb_1, its points b and b_1 are to be imagined close to n and n_1. Let us at first contemplate the equilibrium $F +$ liquid $n +$ vapour n_1 of the binary system BC.

Because we have in this system a temperature between T_K and T_F, between the three phases the reaction: $F \rightleftarrows$ liquid $n +$ vapour n_1 takes place from left to right with increase of volume. We compare now the ternary equilibrium $F +$ liquid $b +$ vapour b_1, wherein b and b_1 differ but little from n and n_1, with the previous system. We then see that as well the formation of vapour from $F +$ vapour b as also the formation of liquid from $F +$ vapour b_1 takes place with increase of volume. According to the rule deduced in communication VI, the sides solid-liquid and solid-vapour of the threephasetriangle must then approach one another on increase of P and separate from one another on decrease of P. We see that the movement of Fbb_1 in fig. 3 is in accordance with this rule.

The occurrence of a point of maximum- or minimumpressure can be easily examined by the reader.

$T_F < T$. We now take a temperature T a little higher than the minimummeltingpoint T_F of the substance F. We then must distinguish two cases, according as the substance expands or contracts on melting. We only take the first case. In a similar way as is deduced for the general case fig. 12 (I), we now find a diagram as fig. 4, wherein the two curves are exphased. Further, it is assumed again that on these curves neither a point of maximum nor a point of minimumpressure occurs. From the deduction of the diagram, it follows that Fa_1 of the threephasetriangle Faa_1 is situated always between Fa and Fh_1. When the points a and a_1 are situated in the vicinity of n and n_1, Faa_1 turns, as is clear from the figure, in such a way on decrease of pressure, that the line Fa goes ahead. When a and a_1 are situated however, in the vicinity of h and h_1, Faa_1 turns on decrease of pressure in such a way that Fa_1 goes ahead. This turning is in accordance with the rules, deduced in communication VI. Let us firstly contemplate the equilibrium $F + L_n + G_{n_1}$ of the binary system BC. Herein the reaction $L_n \rightleftarrows F + G_{n_1}$ takes place from left to right with decrease of volume. Let us now take the system $F + L_a + G_{a_1}$ of which the points a and a_1 are situated in the immediate vicinity of n and n_1. At the formation of vapour from $F + L_a$ the volume will decrease, at the formation of liquid from $F + G_{a_1}$ the volume will increase.

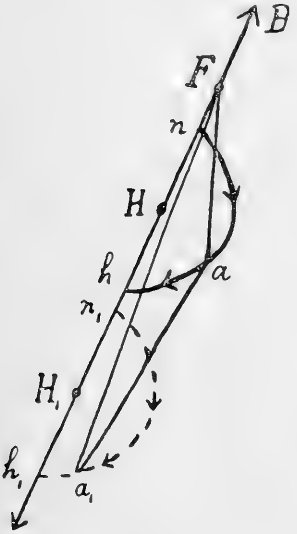

Fig. 4.

According to the rule, deduced in communication VI Faa_1 must on increase of pressure turn in such a way that the line Fa goes ahead. This is in accordance with fig. 4.

In the same way it is deduced that triangle Faa_1, when a and a_1 are situated in the vicinity of h and h_1, must turn on increase of pressure in such a way that the line Fa_1 goes ahead.

Also, however, curves of quite another form may occur, viz. closed curves; these are, therefore, situated completely within the triangle and they are exphased. We imagine e.g. in fig. 12 (I) the component triangle to be drawn in such a way that the point F is situated on the side BC and that the two curves fall within the triangle. Both the curves then show a point of maximum- and a point of minimumpressure. While a binary compound generally may be in equilibrium, in addition to a series of ternary solutions, yet also with two binary solutions, in the above mentioned case, therefore, it is no more the case; now it may be only in equilibrium with ternary solutions.

Drawing the saturationcurves under their own vapourpressure and their corresponding vapourcurves for different temperatures, we may distinguish two principal types; these are represented in fig. 5 and 6. In both the figures, however, the vapourcurves are omitted. At temperatures below the minimum meltingpoint T_F the saturationcurves under their own vapour pressure are circumphased; at T_F the curve goes through F and above T_F they are exphased. In fig. 5 they disappear in a point H on the side, in fig. 6 in a point R within the triangle.

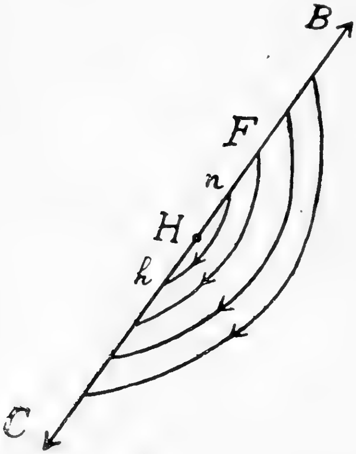

Fig. 5.

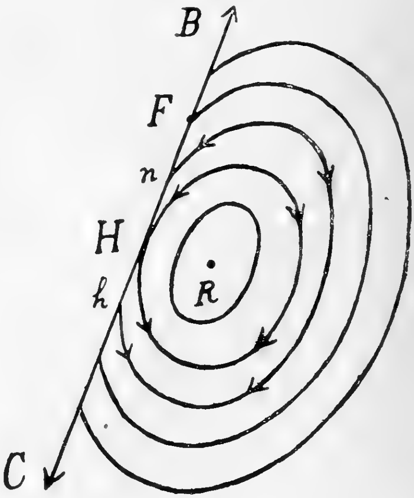

Fig. 6.

At first let us contemplate fig. 5. The arrows indicate the direction in which the pressure increases, therefore, it is assumed that on these curves neither a point of maximum- nor a point of minimum-pressure occurs. When this however is the case, these points form the limit-curve, formerly treated, which is easy to draw in the figure.

The saturationcurves disappear at T_H in the point H; the corresponding vapourcurves disappear at the same time in the point H_1, which is not drawn. We see from fig. 5 that T_H is the highest temperature at which, in the binary system BC, the equilibrium $F+L+G$ can still occur. In this case T_H is also the highest temperature at which in the ternary system the equilibrium $F+L+G$ can still occur.

In fig. 6 the saturationcurve of the temperature T_H does not disappear in the point H; it forms a closed curve, which touches the side of the triangle in a point H. On further increase of temperature it comes completely within the triangle and disappears in a point R. It is evident that these closed curves, and also the not-closed curves, being situated in the vicinity, show a point of maximum- and a point of minimumpressure. In this case, therefore, a limit-curve exists, going through the point R. The curves situated at a greater distance, need not necessarily show this point of maximum and that of minimumpressure.

If it is imagined viz. that these points, on extension of the curves, continue to approach closer to the side BC and that they coincide with this at last; the point of maximumpressure disappears somewhere between H and C, the point of minimumpressure between H and B on the side BC. The limit-curve then terminates in both these points.

Also we see from the figure that the highest temperature (T_R) at which in the ternary system the equilibrium $F+L+G$ may still occur, is higher than T_H.

In figs. 5 and 6 the curves of different temperatures are all drawn in a same plane. Imagining however perpendicular to this plane a temperature axis and the curves to be drawn in space according to their temperature, the saturationsurface of F under its own vapour-pressure arises. In a similar way the corresponding vapoursurface arises.

In the surfaces belonging to fig. 5 the highest points (H and H_1) are situated on the side-plane BCT; in the surfaces belonging to fig. 6 the highest points (R and R_1) are situated within the prism and not on the sideplane BCT.

Deducing the boilingpointcurves for different pressures we refind again the figures 2, 3, and 4 and figures 5 and 6 deduced from these. The arrows must then be drawn however in opposite direction so that in the figs. 2, 3, and 4 T_h is the lowest and T_n the highest temperature at which the equilibrium $F+L+G$ occurs.

We must still contemplate the cases II and III namely that the vapourpressurecurve of the binary system BC shows a point of maximum, or a point of minimum pressure. After the previous general considerations on the occurrence of ternary points of maximum- and of minimum-pressure, this need not to be considered here.

Now we shall contemplate some points more in detail. When F is a binary compound of the composition $0, \beta, 1-\beta$ (therefore $\alpha = 0$)

$$[xr + (y-\beta)s]\,dx + [xs + (y-\beta)t]\,dy = 0 \; . \quad . \quad . \quad . \quad (1)$$

applies to its saturationcurve at a constant T and P.

The liquid curve of the region LG is fixed by:

$$[(x_1-x)r + (y_1-y)s]\,dx + [(x_1-x)s + (y_1-y)t]\,dy = 0 . \quad . \quad (2)$$

We now imagine in fig. 1 that the liquid curve of the region LG is drawn through the point p or q; we now contemplate $\frac{dy}{dx}$ in this point p or q for both the curves. Because in this point $x=0$ and $Lim.\, xr = RT$ it follows for the saturation curve that:

$$\left(\frac{dy}{dx}\right)_{x=0} = -\frac{RT + (y-\beta)s}{(y-\beta)t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and for the liquid curve of the region LG that:

$$\left(\frac{dy}{dx}\right)_{x=0} = -\frac{\left(\frac{x_1}{x}-1\right)RT + (y_1-y)s}{(y_1-y)t} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From (3) and (4) it follows that the tangents on both the curves in the point p have usually a different position, so that the two curves do not come in contact with one another. When (3) is accidentally equal to (4), the two curves touch one another in p or q. This will be the case when:

$$y_1 - y = \left(\frac{x_1}{x} - 1\right)(y-\beta) \quad \text{or} \quad \frac{x_1}{x} = \frac{y_1-\beta}{y-\beta} . \quad . \quad . \quad . \quad (5)$$

Later we shall see that in this case their point of contact p or q is then also a point of maximum- or of minimumpressure of a saturationcurve under its own vapour pressure or of a boiling point curve.

In order to find the saturationcurve under its own vapourpressure we put in (8) and (9) (II) $\alpha = 0$. We obtain:

$$[xr + (y-\beta)s]\,dx + [xs + (y-\beta)t]\,dy = AdP \quad . \quad . \quad . \quad (6)$$

$$[(x_1-x)r + (y_1-y)s]\,dx + [(x_1-x)s + (y_1-y)t]\,dy = CdP \quad . \quad (7)$$

In the terminating point of this curve on the side BC (therefore in the points h and n of figs. 2, 3, and 4), $x = 0$. We find from (6) and (7):

$$\frac{1}{RT} \cdot \left(\frac{dP}{dx}\right)_{x=0} = \frac{y_1 - y - (y-\beta)\left(\frac{x_1}{x} - 1\right)}{(y_1-\beta)V + (y-y_1)v + (\beta-y)V_1} \quad . \quad . \quad (8)$$

In order to find the boilingpointcurve we must substitute in (6) and (7) AdP by $-BdT$ and CdP by $-DdT$. We then find:

$$\frac{1}{RT} \cdot \left(\frac{dT}{dx}\right)_{x=0} = -\frac{y_1 - y - (y-\beta)\left(\frac{x_1}{x} - 1\right)}{(y_1-\beta)H + (y-y_1)\eta + (\beta-y)H_1} \quad . \quad . \quad (9)$$

From (8) it follows that in a terminatingpoint of the saturation-curve under its own vapourpressure on one of the sides (points h and n of fig. 2, 3, and 4) $\frac{dP}{dx}$ has a definite value different from zero so that the pressure is in the terminatingpoint neither a maximum nor a minimum. The same follows from (9) for the temperature in the terminatingpoint of a boilingpointcurve.

In the binary system BC the relation between a change of P and T in the equilibrium $F + L + G$ is fixed by:

$$\left(\frac{dP}{dT}\right)_{x=0} = \frac{(y_1-\beta)H + (y-y_1)\eta + (\beta-y)H_1}{(y_1-\beta)V + (y-y_1)v + (\beta-y)V_1} \quad . \quad . \quad . \quad (10)$$

From (8), (9), and (10) it now follows that:

$$\left(\frac{dP}{dx}\right)_{x=0} : \left(\frac{dT}{dx}\right)_{x=0} = -\left(\frac{dP}{dT}\right)_{x=0} \quad . \quad . \quad . \quad . \quad (11)$$

In order to see the meaning of this we imagine a graphical representation of P and T of the binary equilibrium $F + L + G$. We will call that part of the P,T-curve on which the pressure increases when raising the temperature, the ascending branch, the part on which the pressure decreases when lowering the temperature the descending branch. In the ascending branch $\frac{dP}{dT}$ is positive, in the descending branch it is negative; from (11) it follows, that $\frac{dP}{dx}$ and $\frac{dT}{dx}$ have in the ascending branch the opposite sign and in the descending branch the same sign. We find therefore:

When the binary equilibrium $F+L+G$ is situated in an ascending branch of its P,T-curve, addition of a third substance has an opposite influence on the pressure (at constant temperature) and on the temperature (under constant pressure). When addition of a third substance e. g. increases the pressure (at constant T) it will decrease the boiling point (under a constant pressure).

When the binary equilibrium $F+L+G$ is situated in an descending branch of its P,T curve addition of a third substance has the same influence on the pressure (at constant T) and on the temperature (under constant P). When addition of a third substance increases for instance the pressure (at constant T) it will also increase the boilingpoint (under constant P).

These rules are also true when F is instead of a combination one of the components e.g. B or C.

We will now still examine, in what case the pressure (at constant T) of the binary equilibrium $F+L+G$ is increased or decreased by addition of a third substance. We may express this also in the following way: in what case does the pressure along a saturationcurve under its own vapourpressure from one of its terminatingpoints (h and n in figs. 2, 3, and 4) increase or decrease?

We take for this formula (8), which indicates the relation between the change of pressure dP and the quantity dx of the new substance.

Between the 3 phases of the binary equilibrium $F+L+G$ a reaction may always take place. We let the reaction take place in such a way that 1 quantity of vapour occurs. The occurring change of volume we call ΔV. The denominator of (8) becomes then $(\beta-y)\,\Delta V$, so that we may write:

$$\frac{1}{RT}\cdot\left(\frac{dP}{dx}\right)_{x=0}=\frac{1}{\Delta V}\cdot\left(\frac{x_1}{x}-\frac{\beta-y_1}{\beta-y}\right) \quad . \quad . \quad . \quad . \quad (12)$$

We now take the ternary equilibrium $F+L+G$ wherein L and G contain still only a little of the third substance. The line solid-liquid (Fa or Fb in figs. 2—4) then intersects the X-axis (side CA of the componenttriangle) in a point at the distance S from C. The line solid-gas (Fa_1 or Fb_1 figs. 2—4) intersects this X-axis in a point at the distance S_1 from C. We take S and S_1 positive, when the points of intersection are situated on the right, negative, when they are on the left of C. S and S_1 are fixed by

$$S=\frac{\beta x}{\beta-y} \qquad S_1=\frac{\beta x_1}{\beta-y_1} \quad . \quad . \quad . \quad . \quad (13)$$

Substituting $\beta-y$ and $\beta-y_1$ from (13) in (12) we find:

$$\frac{1}{RT}\left(\frac{dP}{dx}\right)_{x=0} = \frac{1}{\Delta V} \cdot \frac{x_1}{x}\left(1 - \frac{S}{S_1}\right) \quad . \quad . \quad . \quad . \quad (14)$$

From this relation it follows that the sign of the change of pressure depends on the sign of ΔV. Now ΔV is almost always positive for the binary equilibrium $F + L + G$ and negative only between the points F and H (figs. 5 and 6). Further it follows that the sign of the change of pressure is not fixed by the ratio $x_1 : x$ (the partition of the third substance between gas and liquid), but by the ratio $S : S_1$; therefore this is by the ratio of the parts which the lines Fa and Fa_1 or Fb and Fb_1 cut off from the X-axis. We may consider S and S_1 also as the perspective projections of x and x_1 from the point F on the X-axis. We shall call for that reason S the perspective concentration of the new substance in the liquid, and S_1 that of the new substance in the vapour. These perspective concentrations can be as well positive as negative.

From (14) we can now easily deduce for the addition of a new substance:

1. The formation of vapour in the binary system $F + L + G$ takes place with increase of volume ($\Delta V > 0$).

When in liquid and vapour the new substance has perspective concentrations of opposite sign, the pressure increases.

When in liquid and vapour the new substance has perspective concentrations of the same sign, the pressure increases, when the perspective concentration (apart from the sign) of the new substance is greater in the vapour than in the liquid, the pressure decreases when the reverse is the case.

2. The formation of vapour in the binary system $F + L + G$ takes place with decrease of volume ($\Delta V < 0$).

The changes of pressure take place in opposite direction as sub 1. It may be considered with this, that $\Delta V < 0$ is the case only between T_F and T_H, therefore between the minimum-melting point of F and the point of maximum-temperature of the binary system $F + L + G$.

When we take a threephasetriangle in the vicinity of the side BC, its angle F is either a little greater than 0° (Faa_1 and Fbb_1 in fig. 2) or a little smaller than 180° (Fbb_1 in fig. 3). We will call the threephasetriangle in the first case acute-angled, in the second case obtuse-angled. We may express the previous rules also in the following way:

1. The formation of vapour in the binary system $F + L + G$ takes place with increase of volume ($\Delta V > 0$).

An obtuse-angled threephasetriangle moves on increase of pressure both its sides solid—liquid and solid—gas towards each other and on decrease of pressure away from each other.

An acute-angled threephasetriangle moves on increase of pressure with the side solid—gas ahead, on decrease of pressure with the side solid—liquid ahead.

2. The formation of vapour in the binary system $F+L+G$ takes place with decrease of volume ($\Delta V<0$).

The triangles move in the opposite direction as sub 1..

We see that the position of the threephasetriangles in the figs. 2—4 are in accordance with these rules.

In a similar way as we have converted (8) into (14), we may deduce from (9):

$$\frac{1}{RT^2}\cdot\left(\frac{dT}{dx}\right)_{x=o}=-\frac{1}{\Delta W}\cdot\frac{x_1}{x}\left(1-\frac{S}{S_1}\right)\quad .\ .\ .\ .\quad (15)$$

ΔW represents here the heat that is required to form 1 quantity of vapour. The same rules as above may be deduced from this, we must then however replace increase of pressure by decrease of T and decrease of pressure by increase of T.

We should have been able to deduce the rules, deduced above, for the movement of the threephase triangles on change of pressure and temperature, from the rules found in Communication V and VI.

As a particular case of the above-discussed we may put the question: what influence has a third substance on the binary equilibrium $F+L+G$ when this is situated in the point of maximum sublimation or in the minimummelting point of the substance F.

In the point of maximum sublimation the binary vapour has the same composition as the substance F_1; therefore $y_1=\beta$. The vapour-saturationcurve under its own vapour-pressure goes through the point F (in this transition-case between the figures 2 and 3 n_1 coincides therefore with F). When we put in (8) and (9) $y_1=\beta$, we find:

$$\frac{1}{RT}\cdot\left(\frac{dP}{dx}\right)_{x=0}=\frac{1}{V_1-v}\cdot\frac{x_1}{x}\ \text{and}\ \frac{1}{RT^2}\cdot\left(\frac{dP}{dx}\right)_{x=0}=-\frac{1}{\Delta W}\cdot\frac{x_1}{x}.\quad (16)$$

Herein V_1-v is the increase of volume on sublimation, ΔW the heat of sublimation of the substance F. Therefore, both are positive. From (16) it now follows:

when the equilibrium $F+L+G$ is situated in the point of maximum sublimation of the substance F, addition of a third substance will increase the pressure (T constant) and decrease the temperature (P constant).

In the minimum-melting point the binary liquid has the same composition as the substance F, therefore $y=\beta$. The saturationcurve under its own vapour-pressure goes therefore through point F. (In this transition-case between figs. 3 and 4, n, therefore, coincides with

F). When we put in (8) and (9) $y=\beta$, then it follows:

$$\frac{1}{RT}\cdot\left(\frac{dP}{dx}\right)_{x=0}=\frac{1}{V-v} \text{ and } \frac{1}{RT^2}\cdot\left(\frac{dP}{dx}\right)_{x=0}=-\frac{1}{\Delta W}. \quad . \quad (17)$$

Herein $V-v$ is the increase of volume on melting, ΔW the heat of melting of the substance F. $V-v$ can be as well positive as negative, ΔW is always positive. From (17) it now follows that:

when the equilibrium $F+L+G$ is situated in the minimum-meltingpoint of the substance F, addition of a third substance will increase the pressure (T constant), when the substance melts with increase of volume ($V>v$) and decrease when the substance melts with decrease of volume ($V<v$). The temperature (P constant) is lowered.

We may express the above-stated also in the following way:

from F the pressure increases along the vapoursaturationcurve under its own vapour-pressure going through F and the temperature decreases along the boilingpointcurve going through F.

From F the pressure increases along the saturationcurve under its own vapourpressure going through F, when F melts with increase of volume and the pressure decreases when F melts with decrease of volume. Along the boilingpointcurve going through F the pressure decreases from F.

Also we should be able to examine what influence has a third substance on the binary equilibrium $F+L+G$, when this is situated in the point of maximum temperature (point H in figs. 5 and 6) or in the point of maximum pressure of its P,T-curve. We refer to this later.

(To be continued).

Physiology. — "*The effect of subcutaneous turpentine-injections on the chemotaxis of remote places.*" By Prof. H. J. Hamburger. After experiments by Dr. J. Buitenhuis.

(Communicated in the meeting of November 29, 1913).

On a former occasion the attention was drawn to the favourable effect of slight amounts of turpentine on the rapidity of phagocytosis.[1]) In a dilution of 1 : 100.000 an increase was found of 24.7 °/₀ and even in a dilution of 1 : 500.000 an increase of 16 °/₀.

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[1]) Hamburger, de Haan and Bubanovic: On the effect of Chloroform, Iodoform and other substances dissoluble in fat, on Phagocytosis. Proceedings of the Meeting of Jan. 28, 1911, p. 913.

Elsewhere [1]) we have pointed out that the result agrees with a great number of clinical experiences. The gynaecologist FOCHIER from Lyons for example has successfully applied turpentine in the treatment of puerperal fever. For this purpose he injects turpentine under the skin which gives rise to an abscess in this place and the fever soon disappears.

FOCHIER thinks that the abscess attracts the noxious substances which cause the fever, thus rendering them inactive. He speaks of an "Abscès de fixation".

In veterinary circles this treatment has caused much enthusiasm. The pneumonia (crupposa) of horses is at present chiefly and successfully treated with turpentine-injections. In the veterinary School at Utrecht for instance J. J. WESTER adopted this method with excellent results.

He justly doubts, however, whether we are right in assuming an "abscès de fixation". No plausible reasons can be adduced for this hypothesis. Therefore he is more inclined to attribute this favourable result to an improved action of the heart.

It seems not impossible to me that this factor has to be reckoned with. But it is certainly not the only one; for in Denmark the same treatment is successfully applied to chronic mastitis of the cow. And a better action of the heart, such as is often necessary in pneumonia, would be of no avail here.

Therefore we have asked ourselves if this favourable effect of turpentine may not be explained by assuming that this substance enters the circulation from the place of injection as a weak solution, thus stimulating the phagocytosis also in the hearths of the disease, which would assist the curative process.

From a technical point of view, however, it is very difficult to investigate the degree of phagocytosis in an inflamed centre and to determine thus whether the activity of the phagocytes has increased.

This seemed possible, however, by chemotactical experiments.

For this purpose, just as in the case of Calcium, two methods were adopted [2]).

The first method consisted in capillary tubes, filled with an extract of coli bacteria, being placed under the skin of one of the hind legs

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[1]) HAMBURGER: Physikalisch-chemische Untersuchungen über Phagozyten. Ihre Bedeutung vom allgemein biologischen und pathologischen Gesichtspunkt. Wiesbaden, J. F. BERGMANN, 1912, p. 159.

[2]) Cf. HAMBURGER. The effect of slight quantities of Calcium on the motion of the phagocytes. Proceedings of the Meeting of May 28, 1910.

of a rabbit at the inside of the thigh. These extracts also contained traces of turpentine.

Similar tubes were placed at the other hind leg with the same contents, but without turpentine.

After 20 hours the leucocyte columns, which owing to chemotaxis had entered the tubes, were measured. This rendered it possible to establish if, and if so, to what extent, turpentine had promoted chemotaxis and stimulated the phagocytes.

The second method consisted in 0.3 cc. of turpentine being injected under the breast skin of some rabbits; it was then determined if a greater amount of leucocytes had entered the capillary tubes with coli-extract, than if the same rabbits had been injected with 0.3 cc. of NaCl-solution instead of 0.3 cc. of turpentine.

Before stating the results obtained on the effect of turpentine we shall communicate a series of experiments which were made to ascertain the degree of accuracy of the method. In four rabbits capillary tubes are placed right and left under the skin of the leg. These tubes are filled with the same extract of coli-bacteria in NaCl 0,9 $^0/_0$.

The following table will require no further explanation.

TABLE I.
Effect of extract of Coli-bacteria on chemotaxis.

		Left leg. Extract of Colibacteria in 0.9$^0/_0$ NaCl	Right leg. Extract of Colibacteria in 0.9$^0/_0$ NaCl	
Rabbit 1	Total of 4 leucocyte-columns after 2 hours	4.1 mm	4.5 mm	+ 0.4
„ 2	„	6.3 „	5.5 „	— 0.8
„ 3	„	5.6 „	5.5 „	— 0.1
„ 4	„	5.6 „	5.2 „	— 0.4

This table shows that the greatest deviation amounts to 0.8, whilst the deviation in all 4 rabbits together only comes to 0,9 mm.

First method.

Under these circumstances it could be established now, to what extent an addition of turpentine to an extract of B. Coli in NaCl-solution would affect the degree of chemotaxis. [1])

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[1]) The technical details were about the same as those we described in Virchow's Archiv B. CLVI p. 329, 1899 and in "Physik. Chemische Untersuchungen über Phagozyten". Bergmann 1912. p. 94 foll. Only instead of cork paraffin was used to keep the capillary tubes in their places.

For this purpose we used capillary tubes with extract of bacteria-coli in NaCl 0,9 %, in which 1 : 100.000 turpentine had been dissolved.

In each rabbit 4 capillary tubes with and 4 without turpentine were placed on one side under the skin of the leg. After 20 hours they were taken away, and the lengths of the leucocyte-columns were measured.

Table II gives the results of this experiment.

TABLE II.

Effect of extract of Coli-bacteria on chemotaxis.

		Left leg. Coli-bacteria extract in 0.9% NaCl	Right leg. Coli-bacteria extract in 0.9% NaCl +1:100.000 turpentine	
Rabbit 5	Total of 4 leucocyte-columns after 20 hours	4.8 mm	4.6 mm	— 0.2
„ 6	„	3.2 „	4.8 „	+ 1.6
„ 7	„	4.— „	5.1 „	+ 1.1
„ 8	„	4.8 „	6.4 „	+ 1.6
„ 9	„	4.1 „	5.2 „	+ 1.1
„ 10	„	6.9 „	7.1 „	+ 0.2
„ 11	„	2.2 „	3.1 „	+ 0.9

In 6 of the 7 cases, therefore, the turpentine in a concentration of 1 : 100.000 has stimulated the chemotaxis.

In order to investigate if rabbit 5 made an exception to the rule, or if a mistake had been made in the experiment, the experiment was repeated with the same rabbit in the same places. It was found then that the values became 5,1 and 6.8 respectively. In this case too an increased chemotaxis has, therefore, been established.

We subjoin an experiment with a weaker turpentine-solution viz. with turpentine 1 : 500.000. Cf. table III.

These results show that an addition of turpentine 1 : 500.000 *has had a much more favourable effect still on the chemotaxis than turpentine* 1 : 100.000.

Elsewhere[1]) a more detailed account of the experiments will be published.

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[1]) In the dissertation (Bern) of Mr- J. BUITENHUIS.

TABLE III.

Effect of coli-bacteria-extract on chemotaxis.

		Left leg. Extract of coli-bacteria in 0.9% NaCl	Right leg. Extract of coli-bacteria in 0.9% NaCl + 1:500.000 turpentine	
Rabbit 12	Total of leucocyte-columns after 20 hrs	4.9 mm	6.4 mm	+ 1.5
„ 13	„	4.5 „	7 „	+ 2.5
„ 14	„	4.2 „	5.8 „	+ 1.6
„ 15	„	3.6 „	5.4 „	+ 1.8
„ 16	„	4.4 „	4.8 „	+ 0.4
„ 17	„	6.1 „	8.1 „	+ 2
„ 18	„	6.2 „	7.4 „	+ 1.2

Second method.

As we observed before, the second method of investigation consisted in turpentine being injected subcutaneously in the lower chest to enable it to spread through the body with the blood, thus entering also into the lymph of the hind leg, where tubes with extracts of bacteria in NaCl 0,9 % had been placed. The experiment showed that turpentine entered the system but slowly. For when after 7 days the injectionplace was opened, the mucous mass which came out still strongly smelled of turpentine. Turpentine, indeed, does not dissolve readily in watery fluids.

Since in different rabbits the chemotactical action is not the same, the columns of each rabbit were measured without anything being injected. When this had been determined half the rabbits were injected under the breast with 0.3 ccm. of turpentine and the other half, as a test, with 0.3 ccm. of NaCl-solution 0.9%.

Five or six hours after injection the capillary tubes were placed under the skin and they were removed after 20 hours. The following table gives a survey of the results obtained.

Now if we compare the total of the differences of 2, 4, 6, 8 and 10 which comes to **+ 6,1** mm. with the total of the differences of 1, 3, 5, 7 and 9, which amounts to **— 0,1**, *then it appears that the subcutaneous injection of turpentine has evidently stimulated the chemotaxis.*

It must therefore be concluded that, in accordance with our hypo-

TABLE IV.

Effect of the subcutaneous injection of turpentine on chemotaxis.

	Length of 4 leucocytecolumns			
	Left leg. Before the injection of NaCl or of turpentine	Right leg. After the injection of 0.3 cc. of turpentine or NaCl 0.9%		Difference
Rabbit 1	6.6 mm	Turpentine	7.4 „	+ 1.8 (Turpent.)
„ 2	6.6 „	NaCl	5.7 „	— 0.9 (NaCl)
„ 3	6.3 „	NaCl	5.9 „	— 0.4 (NaCl)
„ 4	5.8 „	Turpentine	5.8 „	0 (Turpent.)
„ 5	4.8 „	NaCl	5.5 „	+ 0.7 (NaCl)
„ 6	6 „	Turpentine	7.2 „	+ 1.2 (Turpent.)
„ 7	5.1 „	NaCl	6.4 „	+ 1.3 (NaCl)
„ 8	4.4 „	Turpentine	7.1 „	+ 2.7 (Turpent.)
„ 9	4.9 „	NaCl	4.3 „	— 0.6 (NaCl)
„ 10	5.8 „	Turpentine	6.2 mm	+ 0.4 (Turpent.)

thesis, turpentine has gradually been removed from the place of injection to different parts of the body, also to the blood-vessels of the leg where turpentine was imparted to the lymph, which had a favourable effect on the chemotaxis.

Repeated injection of turpentine in diluted solution.

If this view was correct then it might be expected that an injection of turpentine in a diluted solution, if repeated a few times, would likewise effect an increased chemotaxis.

This would, moreover, prove that the salutary therapeutic effect of the turpentine would be entirely independent of the notion "abscès de fixation". At the same time this might lead to the application of turpentine in human pathology being resorted to more frequently, for in spite of the success obtained by FOCHIER and others after him, it is a wellknown fact that the subcutaneous injection is, if possible, avoided because the sterile abscess, caused by it, is so extremely painful. Indeed when we see how, after the abscess has existed for some days, the mass taken out, which still smells of turpentine, is a mucous one, it becomes evident what destruction the turpentine has caused there.

We investigated therefore whether the chemotaxis could not likewise be stimulated by injecting subcutaneously a solution of turpentine in NaCl 0.9 °/₀ in a concentraton of 1 : 10.000, instead of pure turpentine.

Provisional experiments have indeed shown that this has a favourable effect on chemotaxis. It was not considerable however.

Probably this must be attributed to the ineffective manner in which the experiments were carried out. In the first place too little was injected viz. only 5 times 5 cc. of a turpentine solution of 1 : 10.000, which means only a total amount of 0.0025 cc. of turpentine. But especially too much time elapsed between the injections so that the turpentine injected, had ample opportunity to be secreted in large quantities by the kidneys, whilst the method of injection adopted by FOCHIER creates a reserve of turpentine, from whence turpentine is continually yielded to the circulation.

In subsequent experiments, which, owing to lack of time, could not be carried out as yet, the above-mentioned consideration will be taken into account.

As the technical difficulties attending turpentine-injections are being removed, it will be possible to make use of these injections much more frequently in human pathology; meanwhile it may now be concluded already from the foregoing experiments that turpentine also stimulates chemotaxis in remote places. Further we may infer from the greater mobility of the phagocytes, which is indeed also the foundation of an increased chemotaxis, that in those places the phagocytosis will be stimulated likewise.

Groningen, November 1913. *Physiological Laboratory.*

Botany. — *"Adjustment to light in oats"* By W. H. ARISZ. (Communicated by Prof. WENT).

(Communicated in the meeting of November 29, 1913).

§ 1. *Introduction.*

In this preliminary communication there will be considered a number of phenomena which are generally grouped as adjustment phenomena (German: "Stimmung"). By functional adjustment is usually meant the state of an organ which determines the effect with which the latter reacts to a stimulus of a certain strength.

A change in adjustment is therefore made evident by a change in the reaction to a stimulus of the same intensity. Thus it has been known for a long time that plants grown in the light do not show the same sensitiveness to unilateral illumination as etiolated ones. Pringsheim [1]), in a series of investigations, has attempted to obtain a more detailed knowledge of these processes and quite recently there appeared a paper by Clark [2]) which, as an extension of Pringsheim's work, possesses in many ways points of contact with the results about to be described. Clark's conclusions and my own differ on a fundamental point, namely the validity of the energy law for negative reactions.

There are also striking differences with regard to our observations on the influence of omnilateral preliminary and after-illumination. Since Clark's paper fortunately appeared before the close of the present investigation, I have been able to test his results by control experiments, which, at least with regard to the influence of omnilateral after-illumination, have sufficiently explained the divergence in our results. For a further explanation and for theoretical considerations I must, however, refer to the detailed account of my investigations, about to be published elsewhere.

§ 2. *Method.*

My method is in principle the same as that of Pringsheim and of Clark. These investigators obtained the omnilateral illumination by causing pots with seedlings to rotate on a clinostat round a vertical axis in front of the source of light. The objections to this method are that owing to the excentric position of most of the plants, the latter do not receive equal quantities of light on all sides, while moreover, on account of the large numbers of plants in each pot, they are continually getting into each other's shadow. Owing to the kindness of Prof. Went I was able to use an apparatus specially built for these experiments. It is a kind of multiclinostat, in which 20 pots can rotate simultaneously each on its own axis. The arrangement is such, that when the source of light is one metre from the instrument, the possibility is excluded of the plants getting into each other's shadow. The time for a revolution varies from 4 seconds to 4 minutes, whilst a brake with an electrical contact makes it possible to illuminate during an integral number of revolutions. Since the plants rotate round their own axis, it is possible to use fairly large velocities

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[1]) Cohn's Beiträge Bd. 9. 1909. Bd. 10. 1910.

[2]) Zeitschr. f. Bot. Bd. 5. H. 10. 1913.

without fear of centrifugal force. In the series of experiments now published, the rotation velocity was always 5 sec. The source of light was a NERNST projectionlamp fed by a current maintained constant. The light from the lamp, which was placed outside the dark room, passed through a cooling apparatus with running water and then through a diaphragm into the dark room. By interposing plates of frosted and of milk glass the intensity of the light could be changed in a few seconds. A greater intensity than 450 candles-metre was not obtainable with this lamp at the distance at which the multiclinostat was placed. The experiments described below, with unilateral illumination at greater intensities were carried out with the aid of a projection arc lamp which gave at 1 metre an intensity of 4600 candle-metre power. The numbers referring to the latter illuminations have no claim to great accuracy.

The experiments were carried out in a small dark room in the experimental hothouse of the laboratory. This small space could be maintained at 23° C. by means of an electric heating apparatus and regulator.

§ 3. *Omnilateral fore-illumination followed by unilateral after-illumination*

In order to determine the state of sensitiveness of a plant at a given moment, the plant must be exposed to unilateral illumination at this moment and the resultant reaction must be observed. In the course of the investigation it was found desirable to make a rule of following the process of curvature, for the first two hours. A longer period was not required for after two hours no further phototropic phenomena became visible. The investigation aimed at observing how a plant behaves towards unilateral illumination of various intensities, after previous exposures of varying duration and intensity. In order to determine the state of sensitiveness exactly at the end of the preliminary illumination it is necessary to supply the quantity of energy of the unilateral after-illumination in as short a time as possible. How desirable this is will be seen especially from a consideration of the processes discussed below, affecting the return of sensitiveness. In contradistinction to PRINGSHEIM and to CLARK, I did therefore not always use the same intensity for the unilateral after-illumination as had been employed when the plants were rotating.

On the contrary, an attempt was made to supply the plants in as short a time as possible with a definite amount of energy, which attempt was only limited at the higher amounts by the available supply of light. I have investigated the influence of omnilateral fore-illumination by allowing the plants to rotate for various periods of time at 5 different intensities, of 5.5, 12.1, 25, 100 and 450 candle metre power. The results of the first four series are summarized in tables. Without going into points of agreement and difference, which would require detailed discussion, I here only wish to remark, that Table I is comparable with the investigation of PRINGSHEIM (second paper IV) and that my table III shows agreement with CLARK's figure 2.

It is especially by a consideration of table I, where the preliminary illumination is weakest, namely 5.5 candle metre power, that we can most readily obtain some idea of the influence of omnilateral fore-illumination. A survey of the first six vertical columns of this table, in which the unilateral after-illumination was 22—1000 C.M.S., reveals that a fore-illumination of 100 seconds already requires an after-illumination of 60 C. M. S. to bring about a curvature, whereas after 10 seconds 22 C. M. S. were able to do this. After still longer preliminary illumination not much more energy need be supplied and 120 C. M. S. always gives a definite positive curvature. We may therefore conclude that the sensitiveness has been diminished by the fore-illumination.

A second phenomenon is observed when the amount of the energy of the after-illumination is increased (the last three columns of table I). As I have previously [1]) shown these large amounts of energy (more than 4000 C. M. S.) bring about negative curvatures. Even after brief fore-illumination these negative curvatures occur after large amounts of energy, but now the phenomenon is observed, that after preliminary exposures of 5 minutes or longer, these negative curvatures become feebler, and already after 20 minutes they are no longer obtainable. Then positive curvatures occur, which are extremely feeble at 27000 C. M. S. and become more clearly visible at 13500 and 4500 C. M. S. After 1 hour's fore-illumination the positive curvature is even very marked at 4500 C. M. S.

This second phenomenon, which, as will be explained more fully at the end of this paper, I wish to consider as the typical "adjustment phenomenon" must therefore be formulated as the fact, that after a certain duration of the preliminary exposure, it is no longer possible to obtain negative curvatures at a certain intensity of unilateral after-illumination.

If we compare with this the other tables we find that also at

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[1]) Proc. Kon. Akad. v. Wetensch. Amsterdam Sept. 1913.

Explanation of signs.

+ all plants show definite positive curvature.
++ all plants show strong positive curvature.
0 no plants curved.
— all plants show definite negative curvature.
+? a few plants show slight positive curvature.
—? a few plants show slight negative curvature.

Two different signs placed in the same space e.g. ± means that the reaction after about 1 hour was according to the first of these, after about 2 hours according to the second.

No previous illumination.

No previous illumination	Energy of the unilateral illumination in C. M. S.								
	22	44	60	120	500	1000	4500	13.500	27.000
	+	++	++	++	++	++	±	–	—

TABLE I.

Intensity of the *omnilateral fore-illumination* **5.5 C.M.**

Duration of omnilateral fore-illumination	Energy of the unilateral after-illumination in C. M. S.								
	4 × 5.5 22	8 × 5.5 44	5 × 12 60	10 × 12 120	5 × 100 500	10 × 100 1000	10 × 450 4500	30 × 450 13.500	60 × 450 27.000
10 sec.	+	++	++	++	++	++	±	—	—
100 sec.		0	+?	+	++	++	±	—	—
3 min.			+?	+	++	++	±	—	—
5 min.		0	0	+	++	++	+	—?	—?
20 min.				+	++	++	+	+ 0	+? 0
1 hour			0	+	++	++	++	+	0

TABLE II

Intensity of the *omnilateral fore-illumination* **12.1 C. M.**

Duration of omnilateral fore-illumination.	Energy of the unilateral after-illumination in C. M. S.								
	22	44	60	120	500	1000	4500	13.500	27.000
10 sec.	+	+	++	++	++	++	±	±?	—
36 sec.	0	+?	+	+	++	++	—	±?	—
100 sec.	0	0	0	+?	++	++	±?	—	—
3 min.			0	?	+?	±??	±?	—?	—?
5 min.			0	0	0	+	±?	±?	—?
20 min.				0	+	++	++	++	++
1 hour.				+?	++	++	++	++	++

TABLE III.

Intensity of the *omnilateral fore-illumination* **25 C. M.**

Duration of omnilateral fore-illumination	Energy of the unilateral after-illumination in C. M. S.								
	22	44	60	120	500	1000	4500	13.500	27.000
10 sec.	0	+?		+	+	+	±	—	—
36 sec.				0	+?	+?	—	—	—
100 sec.				0	?	?	—?	—?	—
3 min.				0	0	0	—?	—	—
5 min.					0	0	+?	+	+
20 min.					+	++	++	++	++
1 hour.				0	+	++	++	++	++

TABLE IV.

Intensity of the *omnilateral fore-illumination* **100 C. M.**

Duration of omnilateral fore-illumination	Energy of the unilateral after-illumination in C. M. S.								
	22	44	60	120	500	1000	4500	13.500	27.000
10 sec.	0	0	0	+?	+	++	—	—	—
36 sec.			0	0	0	0	—	—	—
100 sec.			0	0	0	0	—?	-?	—?
5 min.				0	0	0	0	+?	++
20 min.						0	+	+	++
1 hour.						+	++	++	++

these intensities of fore-illumination the sensitiveness to the positive reaction diminishes at first. Whereas at 12.1 C. M. (table II) it was always possible to obtain a positive effect, this is not so at stronger intensities. At 25 C. M. and 100 C. M. (tables III and IV) it is no longer possible to bring about a positive curvature after a fore-illumination of 100 seconds.

Just as in table I the possibility of obtaining negative curvatures disappears with increased duration of the preliminary exposure, we see also from tables II, III, and IV, after a certain period of fore-illumination, that the strongest unilateral after-illuminations no longer bring about negative curvatures. While at 5.5 C. M. the positive curvatures only occur after a fore-illumination of 20 minutes, we see that with more intense fore-illumination strong positive curvatures already occur in plants which had only 5 minutes fore-illumination.

Tables II and III show a further feature to this extent, that with more prolonged fore-illumination smaller quantities of energy suffice to give again a positive reaction, i. e. the plants become as it were more sensitive. The four tables show gradual transition and present a concordant picture. All tables demonstrate the existence side by side of at least two different processes.

In the first place after any preliminary illumination a larger amount of energy is required to bring about a positive reaction. Secondly after a certain duration of the preliminary illumination the capacity of giving negative curvatures is lost more or less completely; after more prolonged fore-illuminations only positive curvatures occur. This second process, the adjustment phenomenon, recalls the phenomena which are known to occur with unilateral illumination of greater duration. In that case also the capacity of giving negative curvatures is lost and after prolonged illumination only positive curvatures appear. Let us therefore first consider unilateral illuminations of great duration.

§ 4. *Unilateral illuminations of great duration.*

A preliminary idea may be obtained from the following table of intensities from 1.4 to about 20000 candle metre power.

TABLE V.

Unilateral illumination.

	Intensity in candle metre power.							
	1,4	5,5	12	100	450	1800	4600	20000
Negative curvature begins at	Always positive	± 4000 C. M. S.					limit not determined; at about ± 10.000 M. C. S. neg.	
Negative curvature no more visible second positive curvature at		9900	18000	90000	135000	72000	± 18000	± 20000
Duration of stimulus for sec. positive curvature		30min.	25min.	15 min.	5 min.	40 sec.	4 sec.	1 sec.

Unilateral illumination according to Clark.

	1,25	5	16	100	400	2500
Negative curvature begins at	500—900	± 900	± 2000—2500			
Second positive curv. begins at	2300	7500	18000	34000	480000	4500000

At 1.4 metre-candlepower only positive curvatures are found, but at each greater intensity there is a larger or smaller range of energy in which negative curvatures occur. Although the accuracy of the determination of the strongest light intensities was not very great, we may nevertheless say that, at all intensities from 5.5 C.M. onwards, there is a range over which negative curvatures are present. At 5.5 C.M. this range is very small, the curvatures which occur are very feeble and a positive one always precedes them. This range first increases at greater intensities and then diminishes again, but even at the greatest intensity employed, namely 20000 C.M., it was possible to obtain a negative curvature after stimulation for about half a second. If we, however, compare with this the values published by Clark for the appearance of a negative curvature, there is a very striking difference. For the first positive reaction the energy law is valid according to Clark, but not for the negative one. The great discrepancy between our figures depends on the phenomena at small intensities. For larger ones Clark agrees in finding the negative reaction at a constant amount of energy, but for feebler intensities he considers that a negative curvature occurs after much smaller amounts of energy. The cause of the discrepancy is Clark's method of working, as I have been able to show by control experiments. A plant which executes a positive phototropic curvature assumes a position in which its apex is stimulated by gravity. When the reaction caused by the last stimulus is stronger than the phototropic one, the plant assumes an upright position, which greatly resembles that due to a negative phototropic curvature succeeding a positive one. For an amount of energy from 500—2000 C. M. S. Clark has mistaken this geotropic erection for negative phototropic curvatures.1) Had he made his plants, after illumination, rotate on a clinostat round a horizontal axis he would have seen no trace of a negative curvature. I desire to emphasize here, that in all my experiments control observations were made on a clinostat; by this means alone it is possible to obtain

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1) Prof. Jost was so kind as to inform me by letter, that Clark never rotated his plants round a horizontal axis on a clinostat.

certainty with regard to the occurrence of a negative phototropic curvature. We have thus to consider the fact that at small intensities no negative curvatures were observed, whereas at greater intensities, as indeed CLARK also found, after stimulation with a definite amount of energy the plants curve negatively. CLARK's observations were entirely at variance with the energy law. The question now arises, whether the facts, as above set forth, necessitate a limitation of the energy law to smaller amounts of energy. It seems to me that from the data obtained for negative curvatures we may not draw the conclusion that the energy law is invalid for small intensities and a long duration of the stimulus. There are so many facts in favour of the general validity of this law that it is safer to assume that the occurrence of negative curvature is *not* entirely dependent on a definite quantity of energy. It is necessary that this quantity should be supplied within a certain time, for otherwise, owing to processes to be discussed below, the effect is so much diminished, that the excitation, which is required for the negative curvature, is no longer reached.

In place of the negative curvature there arises again at all intensities employed a positive one, when the illumination is continued for a longer period. For this second positive curvature also there is a striking discrepancy between CLARK's figures and my own. My figures (as indeed those of CLARK) show convincingly that the occurrence of the second positive curvature is not dependent on a definite quantity of energy.

If we take into consideration the well-known fact, that it is not even necessary to supply this energy unilaterally, but that the latter as PRINGSHEIM has shown, may be partially replaced by an illumination from the opposite side, then the hypothesis presents itself to us that this second positive curvature arises through a process which is independent of the direction of illumination. *This process* results in a *lowering of the excitation.* In this train of thought there is therefore *no essential difference between the first and the second positive curvature.* On further consideration of the tables an additional conclusion may be drawn. We see that the duration of stimulus, i.e. the time during which illumination was necessary to induce the second positive curvature, decreases continuously at greater intensities, that is to say, that *the intensity of the process, through which the excitation diminishes is greater* according as the *quantity of energy supplied per unit of time increases.* We see therefore in unilateral illumination the same process which we have studied as *adjustment phenomenon* with omnilateral fore-illumination. In that case also the action of this process became evident after a certain period of preliminary illumination by the disappearance of the possibility of inducing negative curvatures and the exclusive appearance of positive ones.

§ 5. *The fading phenomenon* (*"Abklingen"*).

Omnilateral preliminary illuminations render possible the closer study of a phenomenon, which is generally called fading of an excitation. By omnilateral stimulation of a plant for a longer or shorter time we obtain as response a certain insensitiveness. We

TABLE VI.

Fading of an omnilateral preliminary illumination.

Time between fore- and after-illumination	Energy of the unilateral after-illumination in C. M. S.								
	22	44	125	250	500	1000	4500	13.500	27.000
at once				0	0	0	—?	—	—
1 min.					+?	+? 0	—	—	—
5 min.			+	+	++	++	++	±?	—
20 min.		+	++	++	++	++	++	+feetle 0	—?
1 hour	+	++	++	++	++	++	+	0	—?
no fore-illumination	+	++	++	++	++	++	±	—	—

During 100 sec. omnilateral fore-illumination with an intensity of 25 C. M.

TABLE VII.

Fading of an omnilateral preliminary illumination.

Time between fore- and after illumination	Energy of the unilateral after-illumination in C. M. S.								
	22	44	125	250	500	1000	4500	13.500	27.000
at once				0	+	++	++	++	++
1 min.				+?	+	++	++	++	++
5 min.			+?	+	++	++	++	++	+
20 min.		+?	++	++	++	++	++	+	±?
1 hour	+?	+	++	++	++	++	++ +	±? 0	—?
no fore-illumination	+	++	++	++	++	++	±	—	—

During 20 minutes omnilateral fore-illumination with an intensity of 25 C. M.

can then see how this insensitiveness gradually disappears again; for this purpose the plant must be left in the dark for some time and the slight residual sensitiveness which remains at that moment must be determined by observing the magnitude of the reaction to a given stimulus. In tables VI and VII the values are given relating to a preliminary illumination of 25 candle-meter power during 100 secs. and 20 mins. respectively (see also table III).

From table VI we see that the possibility of obtaining positive curvatures has returned after only one minute has elapsed between the end of the omnilateral illumination and the beginning of the after-illumination. After 1 hour the original sensitiveness for the positive reaction has returned more or less completely. It is however remarkable that at 4500 C. M. S. after an interval of 5 mins. between fore- and after-illumination no negative curvature occurs again, but instead a strong positive one. We see that here also through the omnilateral illumination during 100 secs. the adjustment process has been put into action, which process has continued *in the dark* and resulted in the large quantity of energy giving not a negative but a positive curvature. But the intensity of this process also diminishes in the long run, so that after 60 minutes the negative reaction again begins to be evident.

In table VII we see the return of the sensitiveness for positive curvature as well as the possibility of a negative reaction. In this case, however, neither the original sensitiveness for positive curvatures, nor that for negative ones is completely reestablished after 1 hour.

§ 6. *Omnilateral after-illumination.*

Following Pringsheim, I investigated together with omnilateral fore-illumination, the influence of an omnilateral after-illumination. The simplest case imaginable, with two successive illuminations, is that of a brief illumination from one side followed by one of equal strength from the opposite side. Then the result is that the plant remains straight. If there is an interval between the two exposures even of only 2 minutes, the curvatures occur separately, so that there is first a curvature in the direction of the first exposure and then in that of the second.

TABLE VIII

105 C.M.S. (7×15)	immediately afterwards in the opposite direction 105 CMS (7×15).	No curvature.
1 min.	„	No curvature
2 min.	„	apex curves first one way, then the other way
4 min.	„	first one way, then slightly the other way
8 min.	„	first one way then strongly the other way

Clark also paid attention to bilateral illumination and since his results differ from my own, I made a series of observations, collected here in table IX, for special comparison with his figure 7. This table refers to successive illumination from two sides with an intensity of 16 candle metre power. After the first exposure the plants were turned through 180° and illuminated from the opposite side. It is found that as long as a certain interval elapses between the beginning of the two stimuli, each is expressed independently. If for instance the illumination is first for 60 sec. from one side, and is then followed at once by the same quantity of energy from the opposite

TABLE IX.

Successive illumination from two sides.

Duration of the first exposure.	Duration of the second exposure					
	10 sec.	30 sec.	60 sec.	90 sec.	180 sec.	600 sec.
30 sec.	+	0	—	—	—	—
60 sec.	+	+	±	±?	—	—
90 sec.	+	+	±	±?	—	—
180 sec.	+	±?	±	±	±	±
300 sec.	±	±	±	±	±	±
600 sec.	±	±	±	±	±	± +?

Intensity of both exposures 16 candle metre power.
+ signifies curvature in the direction of the first illumination.
— signifies curvature in the direction of the second illumination.

TABLE X.

Unilateral illumination followed by omnilateral after-illumination.

Duration of the unilateral fore-illumination	Duration of the omnilateral after illumination			
	35 sec.	100 sec.	300 sec.	600 sec.
30 sec.	++	±	—	— 0
60 sec.	++	±?	±??	—
180 sec.	+	++ top. —	±	—
300 sec.	±	±?	±?	—

Intensity of fore- and after-illumination 12 candle metre power.
+ signifies curvature in the direction of the first (unilateral) illumination.
— signifies curvature in a direction opposite to that of the first illumination.

side, the two curvatures occur *separately one after the other*. CLARK makes no mention of the first occurrence of the curvature in the direction of the first illumination, and this deprives the phenomenon of its surprising feature.

Let us finally consider table X for an *omnilateral* after-illumination. Although carried out with a somewhat weaker intensity, it may very well be compared with CLARK's fig. 4. In this case also CLARK makes no mention of the positive curvature which occurs first and only gives the negative values. Had the after-illumination here not been omnilateral, no new result would have been obtained, but since all sides were afterwards exposed to an equal amount of energy, the phenomenon is somewhat more complicated. We must come to the very plausible conclusion, that after-illumination has not the same effect on all sides, but has a different effect on the side which had already been illuminated unilaterally. This results in a separate production of the curvatures, first in the direction of the first illumination and then in the opposite one. There is not the slightest reason to call a curvature, in a direction opposite to the first illumination, *negative*.

§ 7. *Summary.*

In conclusion a few results of this investigation may be considered in their mutual relationship.

The observations with *bilateral illumination* (table VIII) show, that when we apply to a plant two stimuli by illuminating first one side and then the opposite side, each stimulus results in a visible ipsilateral curvature, as long as a certain time intervenes between the two exposures. This is very marked when the interval between the two inductions is long and less so with progressively shorter intervals until, when the interval is very short, only very slight apical curvatures are seen. This suggests that also when the two sides are illuminated simultaneously, both stimuli would produce a tendency to curve, which tendencies are not expressed because they are simultaneous, equal and opposite, and therefore annul each other.

The phenomena of *omnilateral* illumination are in complete agreement with this. Here also, under certain conditions, there may occur a curvature towards that side, which has had no preliminary unilateral illumination. An *omnilateral illumination* must therefore be regarded as the *summation of unilateral* ones.

A series of experiments, which are not described here, has shown me, that when a plant is illuminated *simultaneously* from two opposite sides with the same intensity, and when the illumination is then continued on one side, results are obtained completely analogous to those with omnilateral instead of bilateral fore-illumination. It need cause no surprise, that with a *bilateral* illumination, the excess which must be given on one of the sides, to obtain an ipsilateral curvature, must be greater, in proportion as the tendency to curvature on the other side is stronger. This is the same phenomenon, which we have observed after an *omnilateral* fore-illumination. The quantity of energy, which had to be given in one direction, in order to obtain a positive curvature, was greater in proportion as the previous illumination was more intense.

There is no reason to regard this so-called smaller sensitiveness of a previously illuminated plant, which only depends on the necessity of overcoming a tendency to curve, as an adjustment phenomenon. Rather should this name be reserved for the process which we have here always called adjustment process. We have been able to observe how it is affected both by unilateral and by omnilateral illumination.

Bilateral illumination can also give some explanation of the fading phenomenon (§ 5).

We saw that, as the intervals between the two opposite illuminations become longer, the curvatures show better. This gives us a new point of view with regard to the fading process, which the omnilateral illumination enabled us to study.

Here, with the time which elapses between the first stimulation (omnilateral fore-illumination) and the second one (unilateral after-illumination), the power of the latter of becoming visible increases. This manifests itself in the phenomenon that, the longer the interval has lasted, the smaller is the amount of energy required to produce a visible curvature. We must therefore assume that the gradual return of the original sensitiveness is the result of the fact that a tendency to curvature can express itself more strongly when a longer period has elapsed since the last stimulation.

Utrecht, Botanical Laboratory.

Chemistry. — *"The Allotropy of Copper"* I. By Prof. ERNST COHEN and Mr. W. D. HELDERMAN.

1. In studying the earlier literature on copper we found certain indications which justified the presumption that this metal is capable of existing in different allotropic modifications. This presumption had been strengthened by the results of our investigations on tin, bismuth, cadmium and zinc.

We will discuss the indications referred to above in our detailed paper in the Zeitschrift für physikalische Chemie; here only two points may be specially mentioned: 1. MATTHIESSEN and VON BOSE[1]) found as early as fifty years ago, that wires of electrolytic copper had changed their electric conductivity (at 0° C.) after having been heated for some time at 100° C. Table 1 illustrates this phenomenon.

TABLE I.

Conductivity	Wire 1 at 0°	Wire 2 at 0°	Wire 3 at 0°
Before heating	99.526	100.021	100.327
aft. heat. 1 day at 100°	99.943	99.971	100.461
» „ 2 days „ 100°	101.097	100.268	100.563
„ „ 3 » „ 100°	101.418	100.524	100.645
„ „ 4 „ „ 100°	101.671	100.656	100.708
„ „ 5 „ „ 100°	101.682	101.075	100.649
„ „ 6 „ „ 100°	--	101.230	100.705
„ „ 7 „ „ 100°	—	101.469	—

2. Even in those cases where pure copper was used, the values given in the literature for the density of this metal differ amongst themselves very considerably.[1])

2. We carried out our experiments in the same way as those described in our paper "On the Allotropy of Zinc".[2])

Electrolytic copper (KAHLBAUM — Berlin, "geraspelt") was brought in quantities of 100 grams each into a porcelain crucible. The pure metal was melted in an electric furnace, some charcoal powder having been added to it. The melted material which showed a brilliant surface was poured out into cylinders made of asbestos-paper. As soon as the metal had solidified, the cylinders were chilled in water and turned into thin shavings on a lathe.

55 grams of this material after having been washed with ether, dilute nitric acid, water, alcohol, ether, and dried in vacuo over sulphuric acid, were put into a pycnometer in order to determine the density at 25° C. We then observed that the water meniscus in

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[1]) POGGENDORFF's Ann. **115**, 353 (1862).

[1]) Compare e g. KAHLBAUM u. STURM, Zeitschr. f. anorg. Chemie **46**, 280 (1905).

[2]) Proceedings **16**, 565 (1913).

the pycnometer was continually falling at constant temperature. The same phenomenon was observed when the experiment was repeated. This indicates that the metal undergoes some change at this temperature.

3. By manipulating very quickly we succeeded in determining the density at 25°.0 We found in two independent experiments:

$$d\frac{25°.0}{4°}\ 8.889 \text{ and } 8.890.$$

Our thermometers had been compared with a standard of the Phys. Techn. Reichsanstalt at Charlottenburg-Berlin.

After having heated the metal during 24 hours at 100° in a solution of coppersulphate no change of density was observed. Repeating this experiment at 25°, we found

$$d\frac{25°.0}{4°}\ 8.899 \text{ and } 8\ 900$$

These experiments prove that there is a transition temperature between 25° and 100° C.

4. In order to fix this temperature more closely we carried out a determination with the dilatometer, using 300 grams of our chilled metal. The dilatometer (bore of the capillary tube 1 mm.) was filled with paraffinoil, which had been heated for some hours in contact with finely divided copper, until there was no more evolution of gasbubbles.

The dilatometer was now kept at different, but constant temperatures.

TABLE II.

Temperature	Duration of measurements in hours	Rise of level in mm.	Rise of level in mm per hour
25°.0	0.5	— 545	— 1090
45 .0	0.2	— 100	— 500
69 .6	0.3	— 148	— 444
71 .5	18	— 53	— 3
72 .0	4	+ 10	+ 2.5
72 .5	11	+ 45	+ 4
73 .0	0.5	+ 6	+ 12
75 .7	0.4	+ 14	+ 36
80 .9	0.4	+ 30	+ 75

We used the electrically heated thermostat, mentioned in our paper on the allotropy of cadmium [1]).

The results are given in Table 2. (Zie p. 630).

5. This table shows that there is a transitionpoint at **71°.7** C. From this we conclude that there exist two allotropic (enantiotropic) modifications of copper. The phenomena may be described by the equation:

$$Cu(\alpha) \overset{71^\circ.7}{\rightleftarrows} Cu(\beta)$$

6. It may be pointed out that the change in the dilatometer has taken place with great velocity notwithstanding the fact that the copper used in this experiment had not been in contact with a solution of coppersulphate. On the other hand there was a large quantity of finely divided metal present. Here, as in the case of bismuth, tin etc, the presence of this powder suffices to accelerate the transitionvelocity very strongly.

7. The following experiment proves that the velocity of the reaction β-copper → α-copper decreases enormously when this powder is not present.

We took 200 grams of electrolytic copper, melted it in an electric furnace and poured the metal into a melting-spoon, where a series of thin rods was formed. These rods were chilled in water and put into a dilatometer which was filled with paraffinoil. The apparatus was kept during 14 days and nights in a thermostat at 25° C. Practically no change occurred. The transition velocity of β-copper into α-copper is several thousand times smaller than if the finely divided metal is present.

This phenomenon explains the fact that objects made of copper disintegrate so slowly in daily life. It is exactly the retardation observed in the experiment described above, which makes possible the use of copper in daily life. We meet here with the same phenomena which have been described already in the case of tin, bismuth, cadmium and zinc.

8. Our experiments prove that we have to consider copper as a *metastable* system ($\alpha + \beta$ copper), which (below 71°.7 C.) is continuously changing into the stable modification (α-copper). The very strongly marked retardations have concealed the allotropic change from the physicists and chemists who have studied this metal in different directions.

9. Dr. CH. M. VAN DEVENTER has been so kind as to call our

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[1]) Proceedings **16**, 485 (1913).

attention to the following curious historical peculiarity: **Theophrast** (a pupil of Aristotle) says in his book ***περὶ πυρός: καττίτερον γάρ φασὶ καὶ μόλιβδον ἤδη τακῆναι ἐν τῷ Πόντῳ πάγου καὶ χειμῶνος ὄντος νεανικοῖ, χαλκὸν δὲ ῥαγῆναι.*** (It is told that tin and lead melted sometimes in the Pontos when it was very cold in a strong winter and that copper was disintegrated).

10. The properties of copper α and β as well as some problems relating to the technical use of copper will be discussed shortly.

van 't Hoff-*Laboratory.*

Utrecht, December 1913.

Chemistry. — *"The metastability of the metals in consequence of allotropy and its significance for Chemistry, Physics and Technics."* By Prof. Ernst Cohen.

1. The research which I have carried out during these last few months in collaboration with A. L. Th. Moesveld and W. D. Helderman, has proved that several metals which until now were only known in one modification are capable of existing in two (or more) allotropic forms. The continuation of these investigations will show if all metals have this property, but we may even already conjecture that this will be the case. A great many observations described in the earlier literature afford evidence in this direction.

2. We were also able to state the fact that the pure metals as we have known them until now are *metastable* systems consisting of two (or more) allotropic forms. This is a consequence of the very strongly marked retardation which accompanies the reversible change of these allotropic modifications both below and above their transitionpoints. Employing certain devices (using the metals in a very finely divided state, adding an electrolyte) it is possible to increase the transition-velocity in such a degree, that the change of the metastable to the stable form occurs within a short time.

As such changes are very often accompanied by marked changes of volume, the material is generally disintegrated.

3. As until now, chemists and physicists have always dealt with the α- and β-form together, *all* the physical constants of metals, which have been determined, refer to the complicated metastable systems. These are entirely undefined as the quantities of the α- and β-modifications they contain are not known.

Now it is known that a special physical property of any substance at a definite temperature and pressure depends on its allotropic condition. H. F. **Weber** [1]) found the specific heat of carbon (at 10° C.)

0.1128 in the form of diamond
0.1604 ,, ., ,, ,, graphite
0.1653 ,, ,, ,, ,, charcoal

Ernst Cohen and E. **Goldschmidt** [2]) found that the density of *white* tin is 7.28, that of *gray* tin 5.8 (at the same temperature) while **Kôtarô Honda** [3]) has stated that the specific magnetic susceptibility ($\chi \times 10^6$) of *white* tin is $+ 0.025$, while that of *gray* tin is $- 0.35$ at the same temperature. Here even the sign is changed. The existing data on the physical constants of metals known until now are thus to be considered as entirely fortuitous values which depend on the previous thermal history of the material used. Those physical constants, which refer to a well defined condition of the metal are so far unknown. In order to determine these, and only these have a definite signification and are reproducible, we shall have to carry out in the future all measurements for the *pure* $\alpha, \beta, \gamma \ldots.$ modifications of the metals.

4. Considering for instance the important part which the specific heats of the metals have played in chemistry and physics during the last few years, it is evident that a revision of these constants is wanted.

5, What has been said about the specific heat holds evidently for every other physical constant. In our paper on the allotropy of bismuth [4]) we pointed out, that numerous phenomena which had been observed in the study of density, electric conductivity (also under pressure) conductivity for heat, melting point, thermoelectric force, the **Hall**-effect etc. and which had not been explained, may find their explanation if the facts recently found are taken into account.

6. In this way a new field of research for chemists as well as for physicists presents itself. Whilst it will be the task of the chemist to prepare the pure modifications and study their physico-chemical properties, the physicist will require to turn his attention to the determination of their physical constants.

7. From a physico-chemical standpoint it will be very important to study the electromotive behaviour of the allotropic modifications mentioned above. The transitioncell of the sixth kind which I

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[1]) Pogg. Ann. **154**, 367, 553 (1875).

[2]) Zeitschrift für physik. Chemie. **50**, 225 (1905)

[3]) Ann. d. Physik **32**, 1027 (1910) ; The Science Reports of the Tôhoku Imp. Univ., Sendai, Japan. **1**, 1 (1912).

[4]) Zeitschr. f. physik. Chemie **85**, 419 (1913).

described several years ago[1]) may be used for this purpose. In this way it will not only be possible to determine the heat of transformation of the modifications, but also to study the equilibrium between the different forms. Several interesting problems may find their solution in this way. I have carried out some preliminary experiments in this direction (with cadmium) in collaboration with Mr. W. D. HELDERMAN.

8. The same may be said if we consider the numerous alloys which have an industrial as well as a scientific interest.

The melting point curves have to be revised, taking into account the allotropy of the components. Quite recently the important part played by the previous thermal history of alloys has been discovered. DIPPEL[2]) has proved that the specific heat of certain alloys is different according as they are chilled or cooled slowly.

In explaining this fact, DIPPEL has not been able to take into account the allotropy of the components of the alloys he experimented with, as our papers on this subject could not at that time be known to him.

9. I hope to report shortly on the problems which have been indicated here. We will then discuss also several phenomena which are observed in industry, the corrosion of metals in contact with water, rusting of iron, the decay of aluminium objects etc.

Utrecht, December 1913. VAN 'T HOFF-*Laboratory*.

Anatomy. — *"On pteric sutures and pteric bones in the human skull"*. By Prof. A. J. P. v. D. BROEK. (Communicated by Prof. L. BOLK).

It is well known that the pteric region of the skull shows different relations in form and extension of the adjacent sutures as well as in the existence of separate bones, the so called pteric bones, ossa epipterica.

In most of the human skulls the parietal and the ala magna of the sphenoid touch in a more or less extensive spheno-parietal suture.

In some skulls the frontal is reached by the temporal bone, then a fronto-temporal suture is formed. In this case we speak of a processus frontalis ossis temporalis.

The configuration of the pteric region can be influenced by the number, form, extension and situation of the pteric bones.

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[1]) Zeitschr. f. physik. Chem. **30**, 623 (1899).

[2]) Ann. d. Physik **42**, 889 (1913).

An examination of the skulls of papuans, brought home by the LORENTZ' expedition from Dutch South New-Guinea, augmented with a number of papuan skulls, sent to me by the military-surgeon DE KOCK from the same district, showed such relations in the pteric region, that made a closer examination necessary.

A study of the concerning literature teaches, that the different investigations on the proc. frontalis as well as on the pteric bones are nearly all of a statistical nature, and do not reckon with the condition of the two opposite sides of the same skull. As a consequence of this way of investigation, the different forms of processus frontalis are always explained in the same way. Only GRUBER [1]) mentions two forms of a fronto-temporal suture.

The examination of 114 papuan skulls drew my attention to three questions, viz. 1 that several forms of proc. frontalis must be discerned. 2 that for the judging of the character of a processus frontalis the two opposite sides of the same skull must be mutually compared and 3 that the processus frontalis and the pteric bones must be compared with each other.

Regarding the first point I observe that two forms of proc. frontalis ossis temporalis must be distinguished. I call these two forms of proc. frontalis type I and type II.

Type I shows a projecting part at the upper border of the squama temporalis, as is seen in figure 1. By prolonging the suture between temporale and the alisphenoid in upward direction, as is done in

Fig. 1.

Fig. 2.

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[1]) GRUBER W. Über die Verbindung der Schläfenbeinschuppe mit dem Stirnbeine. 1874.

figure 1 by a dotted line, it reaches the parietal (vide figure 1). This is **Gruber**'s "mittelbare Verbindung". Type II shows a regular enlargement of the whole squamosal in the direction of the frontal, so, that a fronto-temporal suture is formed. This is **Gruber**'s "unmittelbare Verbindung". A junction of the second type can be combined with a frontal process of the first type.

The number of examined skulls is 114; in 47 I found a fronto-temporal suture i. e. in 41,14 $^0/_0$.

The skulls of the two different kinds are divided as follows.

In 34 cases we have a frontal process of the first type. In 13 cases the two sides of the skull are symmetrical. In 21 the frontal process is only present at one side. 5 of the 13 skulls with symmetrical frontal process show a combination of the first and the second type, so that from the first type 8 are found with the frontal process on both sides, to 21 with the front. proc. on one side; which means that the unilateral presence is much more frequent than the bilateral.

In 13 skulls the second type was found. Of no less than 12 skulls the two sides were symmetrial and only once I found a unilateral enlargement of the squamosal, which proves that the bilateral presence is much more frequent than the unilateral.

In the unilateral presence of a frontal process of the first type I found this process 13 times on the left side of the skull against 6 times on the right one; so the left half of the skull surpasses strongly the right one in this respect.

An investigation of the pteric region of the side of the skull opposite to a frontal process of the first type led to the following facts:

I. Processus frontalis at the left side.
A spheno-parietal suture at the right side in 6 skulls.
An os epiptericum typicum ,, ,, ,, ,, ,, 3 ,,
Several ossa epipterica ,, ,, ,, ,, ,, 1 skull.
A temporal proc. at the frontal ,, ,, ,, ,, 1 ,,

II. Processus frontalis + os epiptericum at the left side.
An os epiptericum-typicum at the right side in 2 skulls.

II Processus frontalis at the right side.
A spheno-parietal suture at the left side in 2 skulls.
An os epiptericum typicum ,, ,, ,, ,, ,, 2 ,,
Several ossa epipterica ,, ,, ,, ,, ,, 2 ,,

A spheno-parietal suture is mostly found at the side opposite to the frontal process (in 8 of 19 cases). This suture is not always situated in the same place. Usually it lies at the level of the sutura squamosa, so that the region of the frontal process is included in the alisphenoïd.

Sometimes the spheno-parietal suture lies at the level of the lower border of the frontal process; so that the region of this process is included in the parietal. The region of the frontal process of one side can be included in the frontal, as is proved by a skull, which presents at the left side a frontal process of the temporal and at the right side a symmetrical temporal process of the frontal.

If at the side opposite to the frontal process one or more ossa epipterica are found, the situation and extension of these bones are equal to those of the frontal process.

We find other relations in the skulls with frontal processus of the second type. Here the enlargement of the squamosal is nearly always absolutely symmetrical.

Only once did I find a second type of frontal process at one side and an os epiptericum typicum at the other one.

I suppose that the question after genesis and significance of the above mentioned two types of frontal processus must be answered as follows.

The proc. frontalis of the first type is to be considered as the homologon of an os epiptericum typicum. Following arguments led me to this opinion.

In the first place it is possible that the region of a unilateral proc. frontalis can be included at the opposite side in one of the surrounding bones (sphenoid, frontal, parietal).

In the second place it must be remembered that the ossa epipterica, which are present at the side opposite to the frontal process, correspond in their extension and situation to this process.

When we find a frontal process together with an os epiptericum at the opposite side, these two correspond with the frontal process.

At last I have to mention the great variability in form and extension of the proc. frontalis. As I will explain further on, we can find that in a skull with a unilateral os epiptericum or ossa epipterica the opposite side shows the same conditions as in a skull with a unilateral processus frontalis of the first type.

The frontal process of the second type, the enlargement of the whole squamosal, could be due to two causes. In the first place we can suppose that merely an enlargement of the squamosal is cause of the exclusion of the alisphenoid from the frontal, in the second place we can imagine that this enlargement is due to the opposition to the squamosal of that part of the alisphenoid which is not cartilagineous preformed, viz. the os intertemporale from Ranke[1]).

Perhaps both ways of enlargement of the temporal in forward direction occur; only ontogenetical and comparative anatomical investigations could make out this question.

Ossa epipterica.

I have brought the ossa epipterica to the following types.

I. Os epipterieum bordering to four bones (frontal, parietal, temporal, alisphenoid): os epipterieum typicum.

II. Os epipterieum, bordering to three bones.

a: frontal, parietal, alisphenoid: os epipt. anterius.
b: parietal, temporal, alisphenoid: os epipt. posterius
c: frontal, parietal, temporal: os epipt. superius
d: frontal, temporal, alisphenoid: os epipt. inferius.

III. Os epipterieum, bordering to two bones; i. e. presenting itself as a sutural bone.

IV. Several ossa epipterica.

Thirty times I found an os epipterieum typicum

in 4 skulls on both sides
,, 15 ,, ,, the right side
,, 11 ,, ,, the left side.

If an os epipterieum typicum is present on both sides of the skull, the two bones are symmetrical in situation and extension.

If an os epipterieum is only present at one side of the skull we find, when examining the other side of the same skull the following cases:

I. Os epipterieum typicum at the right side

a frontal process	at the left side in	4 skulls.
a spheno-parietal suture	,, ,, ,, ,, ,,	5 ,,
a frontal process and an os epipterieum	,, ,, ,, ,, ,,	3 ,,
Several ossa epipterica	,, ,, ,, ,, ,,	2 ,,

II. Os epipterieum at the left side

a frontal process	at the right side in	2 skulls.
a spheno-parietal suture	,, ,, ,, ,, ,,	6 ,,
Several ossa epipterica	,, ,, ,, ,, ,,	1 ,,

This survey proves that the side of the skull, opposite to an os

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[1] Ranke. J. Ueber den Stirnfortsatz der Schläfenschuppe bei den Primaten. Sitzungsber. bayr. Akad. d. Wissensch 1898.

epiptericum typicum can show just the same condition as a skull with a unilateral processus frontalis of the first type.

That in case of a unilateral os epiptericum typicum the right side is predominant to the left one is due to the predominance of the frontal process of the first type on the left side.

If at the side of the skull, opposite to an os epiptericum typicum a spheno-parietal suture is found, then the same rules hold for the situation of this suture as by a unilateral frontal process; that part of the skull that lies symmetrical to the pteric bone can be included as well in the alisphenoid as in the frontal or parietal bone.

II. I found an os epiptericum of the second type in 7 skulls; in one on both sides and symmetrical, in 5 on the right and in one on the left side. This pteric bone was always combined with a frontal process of the first type. For the composition of the pteric region of the opposite side of the skull in a unilateral occurrence of such a pteric bone can be referred to the description of the frontal process.

III. An os epiptericum of this type I found only once in a skull as a little sutural bone in a fronto-temporal suture.

IV. Several ossa epipterica I observed in 4 skulls; always two bone-pieces were present. In 3 skulls they were on the right; in one on the left side.

For the behaviour of the side of the skulls opposite to those with two pteric bones, I refer to the descriptions before mentioned.

All in all I found pteric bones in 42 skulls, or 36.8 °/₀ that is to say in 5 on both sides, in 23 on the right and in 14 skulls on the left side.

This enumeration proves that pteric bones are more often found on the right than on the left side, on the contrary the fusion of the bone pieces in the pteric region with one of the surrounding bones, specially the squamosal, happens more frequently on the left than on the right side.

It is impossible to decide by this study the meaning of the pteric bones.

The frequent occurrence of these separate bone-pieces in papuan-skulls is not favourable for Ranke's theory, saying they ought to be considered pathological.

Ontogenetical and comparative anatomical researches will be necessary to explain this question of the anatomy of human skull.

Physiology. — *"On the formation of antibodies after injection of sensitized antigens."* By L. K. Wolff. (Communicated by Prof. C. Eijkman.) (First Communication).

In 1902 Besredka [1]) communicated about a new way of rendering trial animals immune against pest, cholera, and typhus. This way of immunizing consisted in injecting the animals with the bacilli in question (either dead or alive), the latter being first treated with an antiserum specially prepared for them, and afterwards being again freed from the superfluous serum.

It appeared that by this treatment the animals became immune much sooner than after being injected with nontreated bacilli, that their state of immunity lasted as long, and besides that by this treatment the bacilli had lost their toxical qualities. Since then Besredka's method has been applied to a great many other bacteria, and according to many authors, mostly with good results.

In a report about his method [2]) in 1910 Besredka finishes, saying that it has been shown that sensitizing procures the bacteria with new qualities, so that now they become first class vaccins, vaccins with a reliable, quick, innocuous, and lasting effect.

In defiance of this seem to be experiments by Neisser and Lubowski [3]), von Düngern [4]) and Sachs [5]) [6]).

Neisser and Lubowski examined upon rabbits the production of agglutinins against typhusbacilli, which were loaded with agglutinins on one side, and by injection of nontreated bacilli on the other side. They found that the former had much less effect than the latter.

It must be remarked that their treated bacilli were saturated to a maximum with agglutinins and were then washed out again several times [7]).

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[1]) C. R. de l'Académie des Sciences, 2 June 1902.

[2]) Bulletin de l'Institut Pasteur, 1910, p. 241.

[3]) Centr. f. Bakteriologie I, vol. 30, p. 483.

[4]) Münch, Med. Woch. Schr. 1900, No. 20.

[5]) Centr. f. Bakteriologie I, vol. 30, p. 491.

[6]) I do not here wish to speak about immunizing by means of toxin-antitoxin mixtures, which have again been brought to the fore by the latest investigations of von Behring as to the way of fighting diptheria. For this consult Kretz (Zeitschr. f. Heilkunde 1901, Heft 4) and J. Rehns (C.R. de la Soc. de Biol. 1901, février), who could not bring about immunisation by compensated mixtures, contrary to Babes, who could, and further von Behring's communications (D. Med. Woch. 1913), who found that a mixture reacting neutrally for one kind of animal, could still be toxical for another.

[7]) J. Rehns (C. R. de la Soc. de Biol. 1900, p. 1058) did not find a difference in immunisation power between agglutinated and nontreated bacilli.

Von Düngern has described a single experiment about the immunisation power of red corpuscles of the ox, loaded with amboceptor, upon the rabbit. In his experimenting he found as good as no amboceptor formation.

Sachs has extended these experiments, and he found that the amboceptorformation was a less good one, but that it certainly did exist. He too communicates but one series of experiments with corpuscles saturated to a maximum.

I here do not wish to show the differences between Besredka's experiments and those of the Germans; this I will do in a following communication. But for me this controversy was enough reason to get some more insight into this question by more extensive experiments. Besides, one argument caused me not to consider of general value the result which the German investigators drew from their experiments, viz. that antigens loaded with antibodies possess no or very little immunisation power.

For it is a wellknown fact that, in order to get an immuneserum with a high titre, one must inject antigen in question more than once. The second and following injections are generally given to an animal that already possesses a certain quantity of antibody, even more than is necessary, to saturate the quantity of antigen which is being injected. Now there is not so very much difference between treating an animal for the second time, and injecting antigen + antibody at the same time into a nontreated animal. And from the fact that a second injection of a previously treated animal does possess immunisation power, I considered the opinion of v. Düngern c.s. improbable.

Suchlike experiments have been made by Dr. Thiele according to a communication given by him during a discussion in the bactereological section of the international congress in London. Then my experiments were already in progress.

I started studying the origin of antibodies in rabbits after the injection of heterogeneous red corpuscles loaded more or less with amboceptor. I have especially taken care also to use red corpuscles, loaded with little amboceptor, because it was possible that this would furnish a clue to solve the difference.

As to the technic of the experiments see below:

A great number of rabbits (15—18) were always injected with foreign red corpuscles at the same time. The rabbits had never been treated with the kind of blood in question before. With my later experiments the animals were always first weighed and injected in proportion to their weight. The corpuscles had always been freed from serum by centrifuging and washing them with a saltsolution. After that they were digested for at least half an hour with the antiserum which was beforehand heated to 56°. As, except for a single exception, homologous (rabbits) serums were always used for this aim, the washing away of the antiserum was not necessary in my experiments, and consequently this was not done. Attention was always paid to all the amboceptor being also absorbed.

In order to find out all about the rapidity of the production of the amboceptors, the rabbits were bled from the earveins every two or three days. (Always little, $^1/_2$ ccm. at the utmost). The serum which was in this way obtained, was heated to 56° for half an hour. That is how no allowance was made for the appearance of thermolabile amboceptors.[1] However, as appears from THIELE and EMBLETON's writing, these are never very numerous, and they soon disappear.

The rate of the amboceptor of the various rabbitserums of one day was always defined with the same Guinea pigserum so that the numbers are mutually to be compared. As unity of amboceptor a serum was taken, 1 ccm. of which together with $^1/_{10}$ ccm. complement (fresh guineapigserum) was able to solve 1 ccm. of a 5 % suspension of the corpuscles in question, in half an hour at a temperature of 37°.

In the following list the *A*.-rabbits have been injected with nonsensitized, the *B*.-rabbits with weakly sensitized, the *C*.-rabbits with strongly sensitized red cells. The bloodquantity is unthinned blood; so for 1 ccm. 20 unities amboceptor are equal to 1 dose.

I.

Subcutaneous injection of sheepblood $1^1/_2$ ccm. per k.g. weight.

A nonsensitized
B sensitized with 6.6 dose
C „ „ 100 „

Strength of the sensitized serum: $^1/_{2000}$.
With *C* all was also absorbed.

A

rabbit	after 5 days	after 7 days	after 10 days	after 12 days	after 14 days
121	$^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{500}$	$^1/_{5\;0}$ nearly
122	$^1/_{20}$	dead	intercurrent disease		
123	$^1/_{20}$ nearly	„	„		
124	$^1/_{50}$	$^1/_{100}$	dead		
125	$^1/_{50}$ nearly	$^1/_{200}$	$^1/_{200}$	$^1/_{500}$	$^1/_{500}$

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[1] THIELE and EMBLETON, Z. f. Immunitätsforschung, XX, p. 1.

B					
126	$^1/_{10}$	$^1/_{50}$	$^1/_{100}$	$^1/_{100}$	$^1/_{100}$
127	$^1/_{10}$ nearly	$^1/_{20}$	$^1/_{20}$	died	
128	$<{}^1/_{10}$	$^1/_{20}$	$^1/_{50}$	$^1/_{200}$	$^1/_{200}$
129	$^1/_{10}$	dead			
130	$^1/_{10}$	$^1/_{100}$ largely	$^1/_{200}$	$^1/_{500}$	$^1/_{500}$
C					
131	$<{}^1/_{10}$	$^1/_{20}$	$^1/_{100}$ nearly	$^1/_{20}$	$^1/_{200}$
132	$<{}^1/_{10}$	$^1/_{20}$	—	$^1/_{100}$	$^1/_{200}$
133	$<{}^1/_{10}$	$<{}^1/_{10}$	dead		
134	$^1/_{10}$	—	$^1/_{50}$	$^1/_{50}$	$^1/_{100}$
135	$^1/_{10}$ nearly	$^1/_{10}$ nearly	$^1/_{20}$	$^1/_{20}$	$^1/_{100}$ nearly
136	$<{}^1/_{10}$	$^1/_{10}$ „	$<{}^1/_{10}$	$^1/_{10}$	$^1/_{100}$

Result: Somewhat quicker formation of antibodies when injecting nonsensitized red cells, and besides formation of somewhat higher titre. But the difference is not much.

II.

Intraperitoneal injection of horseblood $^1/_2$ ccm. per kg.

A nonsensitized.
B sensitized with 4 dose
C „ „ 20 „
rabbitserum, strength $^1/_{200}$.

rabbit	after 5 days	after 7 days	after 10 days	after 12 days
A				
11	nearly $^1/_{10}$	nearly $^1/_{20}$	nearly $^1/_{20}$	$^1/_{20}$
45	$<{}^1/_{10}$	$<{}^1/_{10}$	„ $^1/_{20}$	$^1/_{20}$
48	$^1/_{10}$	$^1/_{10}$	„ $^1/_{50}$	$^1/_{20}$
49	$<{}^1/_{10}$	nearly $^1/_{10}$	„ $^1/_{50}$	$^1/_{20}$
60	$<{}^1/_{10}$	$^1/_{10}$	„ $^1/_{20}$	$^1/_{20}$
B				
63	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$
71	$<{}^1/_{10}$	$<{}^1/_{10}$	nearly $^1/_{10}$	$^1/_{10}$
68	$<{}^1/_{10}$	$<{}^1/_{10}$	„ $^1/_{10}$	$^1/_{20}$
67	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$
70	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$
C				
72	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$	$^1/_{10}$
73	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$
76	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$	$<{}^1/_{10}$
78	$<{}^1/_{10}$	$<{}^1/_{10}$	$^1/_{20}$	$^1/_{20}$
79	$<{}^1/_{10}$	nearly $^1/_{10}$	$^1/_{20}$	$^1/_{20}$

Result: with none of the rabbits a high titre is to be found. But the immunisation with the *A* rabbits is distinctly quicker and better than with those of series *B* and *C*. The conduct of the *A* rabbits is much more regular too; with *B* and *C* there are much more individual differences.

III.

Intravenous injection of oxblood 1.6 c.c.m. per k.g.
A nonsensitized.
B $1^1/_4$ dose } rabbitserum strength $^1/_{500}$.
C 25 „ }

rabbit	weight	after 2 days	after 5 days	after 9 days	after 12 days	after 14 days
A						
107	2100	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{200}$ largely
138	2100	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{100}$	$^1/_{200}$ nearly	$^1/_{200}$
109	2000	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{100}$ nearly	$^1/_{100}$	$^1/_{200}$ nearly
140	2100	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{1000}$ nearly
108	2000	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{50}$	$^1/_{100}$ nearly	$^1/_{200}$
B						
114	3200	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{500}$	$^1/_{500}$ nearly	$^1/_{1000}$ nearly
112	2600	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{200}$	$^1/_{200}$ „	$^1/_{100}$
115	2700	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{500}$	$^1/_{500}$ „	$^1/_{200}$
110	2350	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{200}$	$^1/_{200}$	$^1/_{200}$
116	2350	$<{}^1/_{10}$ after	$<{}^1/_{10}$	$^1/_{200}$ after	$^1/_{500}$	$^1/_{1000}$
104	3100	$<{}^1/_{10}$ 4ds.	$<{}^1/_{10}$	$^1/_{200}$ 11days	$^1/_{500}$	$^1/_{1000}$
139	2300	died	anaphylaxis			
103	3300	„				
C						
106	1700	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{100}$	$^1/_{200}$ nearly	$^1/_{100}$
113	2100	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{20}$	$^1/_{100}$	$^1/_{100}$
121	1200	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{50}$	$^1/_{200}$	$^1/_{200}$
142	1700	$<{}^1/_5$	$<{}^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{200}$
125	1350	died	anaphylaxis			
141	1550	„				
93	2200	„				

Summary: No great differences. But now the *B* rabbits (which have been injected with weakly sensitized red cells) are quickest in producing amboceptors.

The *C* rabbits finally lag behind a little, though not much, the *A* and the *B* rabbits reach the same titre on an average. Soon after the injection (5 minutes to $^1/_2$ day) five rabbits died, 2 *B* and 3 *C* rabbits.

Consequently an intravenous injection of the same quantity foreign red cells is much more dangerous when they are loaded with immune serum.

IV.

Intravenous injection $^1/_4$ c.c.m. per k.g. sheepblood.

A nonsensitized.

B sensitized with 4 unities } dogserum, so heterogeneous serum

C „ „ 20 „ } Strength: $^1/_{100}$.

rabbit	Before the injection (The trialserums were not heated)	after 3 days	after 5 days	after 7 days	after 10 days
A					
100	$^1/_5$	$^1/_{10}$	$^1/_{200}$	$^1/_{500}$	$^1/_{1000}$
101	$^1/_5$	$^1/_{10}$ nearly	$^1/_{200}$ nearly	$^1/_{200}$	$^1/_{1000}$
97	$< ^1/_5$	$< ^1/_{10}$	$^1/_{1000}$	$^1/_{1000}$	$^1/_{2000}$
99	$^1/_5$	$< ^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{500}$
98	$< ^1/_5$	$< ^1/_{10}$	$^1/_{200}$	$^1/_{1000}$	$^1/_{2000}$
B					
96	$^1/_5$	$< ^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{200}$
95	$^1/_5$ nearly	$< ^1/_{10}$	$^1/_{500}$	$^1/_{200}$?	$^1/_{500}$
92	$^1/_5$ „	$< ^1/_{10}$	$^1/_{200}$	$^1/_{200}$	$^1/_{500}$
94	$< ^1/_5$	$< ^1/_{10}$	$^1/_{200}$	$^1/_{100}$	$^1/_{1000}$nearly
93	$< ^1/_5$	$< ^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{1000}$
C					
90	$< ^1/_5$	$< ^1/_{10}$	$^1/_{50}$	$^1/_{100}$ nearly	$^1/_{200}$
91	$^1/_5$ nearly	$< ^1/_{10}$	$^1/_{50}$	$^1/_{200}$	$^1/_{1000}$
87	$^1/_5$ „	$< ^1/_{10}$	$^1/_{100}$	$^1/_{200}$	$^1/_{200}$
89	$^1/_5$ „	$< ^1/_{10}$	$^1/_{50}$	$^1/_{200}$ nearly	$^1/_{500}$
88	$< ^1/_5$	$< ^1/_{10}$	$^1/_{100}$	$^1/_{100}$	$^1/_{100}$

Summary: The rabbits treated here had only a small quantity of normalamboceptors.

The *C* rabbits distinctly become immune more slowly than the *A* and *B* rabbits; the latter remain on the same level the first few days; finally the *A* rabbits carry the victory as to titre.

The use of dogserum for sensitizing does not seem to be of any influence here.

V.

Intravenous injection of sheepblood. 1 ccm. each rabbit. (The rabbits had about the same weights, 2—3 kg.). Each group = 2 rabbits.

A nonsensitized.
B $^5/_{12}$ doses
C $^5/_4$ „
D 8 „
E 24 „
F 50 „
G 100 „
H 150 „

} rabbit serum: strength $^1/_{2000}$. The red cells could entirely absorb 150 doses.

rabbit				
A	after 2 days	after 5 days	after 7 days	after 10 days
8	$^1/_{10}$ weak	$^1/_{50}$	$^1/_{100}$	$^1/_{200}$
X	$< {}^1/_{10}$	$^1/_{10}$ weak	$^1/_{100}$ weak	$^1/_{100}$
B				
9	$^1/_{10}$ weak	$^1/_{10}$	$^1/_{200}$ weak	$^1/_{500}$ weak
17	$^1/_{10}$ „	$^1/_{20}$	$^1/_{500}$ „	$^1/_{500}$
C				
12	$< {}^1/_{10}$	$< {}^1/_{10}$	$^1/_{10}$	$^1/_{50}$ weak
R	$< {}^1/_{10}$	$^1/_{10}$ weak	$^1/_{100}$ weak	$^1/_{100}$ „
D				
21	$^1/_{10}$	?	$^1/_{100}$	$^1/_{100}$
33	$^1/_{10}$ weak	$^1/_{20}$	$^1/_{100}$	$^1/_{100}$
E				
24	$^1/_{10}$ weak	$^1/_{10}$	$^1/_{20}$	$^1/_{50}$
18	$^1/_{10}$ „	$^1/_{10}$	$^1/_{100}$	$^1/_{200}$
F				
M	$^1/_{10}$ weak	$^1/_{10}$ weak	$^1/_{50}$ weak	$^1/_{50}$ weak
22	$^1/_{10}$	$^1/_{20}$	$^1/_{20}$	$^1/_{20}$ „
G				
25	$^1/_{10}$	$^1/_{10}$ weak	$^1/_{50}$ weak	$^1/_{100}$ weak
14	$< {}^1/_{10}$	$^1/_{20}$	$^1/_{50}$	$^1/_{50}$ „
H				
16	$^1/_{10}$	$^1/_{20}$	$^1/_{100}$	$^1/_{100}$
15	$^1/_{10}$ weak	$^1/_{10}$ weak	$^1/_{100}$ weak	$^1/_{100}$

As far as results are to be drawn from this series — for the rabbits have not been exactly injected in proportion to the weight of their body—there does not seem to exist a great difference between the various rabbits. The final result is somewhat better with *A* and *B* than with the others; but the differences are small. The strongly sensitized red cells (150 doses!) also had immunisation power.

At last I have made two more series of experiments, upon which I will not dwell at length; with those the rate of amboceptor with all the animals remained too low to be exactly measured, probably by injecting too little blood: in one series no differences were to be found, in the other the nonsensitized blood immunized a little better, but the differences were small.

The final conclusion to be drawn from these series of experiments may now follow:

In general one also succeeds in rousing amboceptors with sensitized corpuscles. The strongly sensitized red cells mostly work less quickly; the serum of the rabbits gets a lower titre! But on a whole the difference is not great, generally smaller than was found by SACHS and VON DÜNGERN.

The weakly sensitized red cells are generally not inferior to the nonsensitized as to immunisation power (in one series they even worked somewhat more quickly); the final result is either the same or a little less. In one series, with the treatment with red cells of ox appeared the danger of intravenous injection of sensitized corpuscles: a number of rabbits died of anaphylaxis. As a rule however, they could well stand the injections. I made one series of experiments with injection (intraperitoneal) of sensitized and non sensitized red cells of ox into rabbits, which a fortnight ago had already had a first injection of red cells of ox, and which now all had an equal titre ($^1/_{200}$). The rabbits that were injected with strongly sensitized corpuscles all five died of anaphylaxis; of those that were injected with weakly and nonsensitized corpuscles three died of five resp. two of five of anaphylaxis.

So I did not continue those experiments.

December 1913. *Laboratory of Path. Anatomy, Amsterdam.*

M

Physiology. — *"On the relation between the quantity of brain and the size of the body in Vertebrates".* By Prof. EUGÈNE DUBOIS. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of November 29, 1913).

It is obvious that, in general, in different species of animals, the relative quantity of brain must be a measure for the degree of the organisation of the nervous system. There are however still other factors influencing the quantity of brain. In the first place the size of the body, but especially also the age and the individual deviations, further possible deviations caused by the living of the animal out of the state of nature.

Of these factors the three last mentioned ones can easily be excluded, the age, by choosing only full grown animals for comparison, the individual deviations, by taking averages, or (which in some cases may be preferred) by choosing individuals representing the norm. Then remains still the factor of the size of the body. Its influence cannot be appreciated by simply calculating the relative quantity of brain. For a long time it has been known already that in this way the required measure for the organisation of the nervous system cannot be found, but on the contrary false relations are obtained. Then Man is indeed not only inferior to some small Monkeys but even to the Mouse. The latter would then be four times better provided with brain than the Brown Rat, and the Cat five times better than the Tiger or the Lion.

In general we find, not only in Mammals, but in all Vertebrates, that the smaller species of closely allied animals, relatively to the weight of their bodies, have a great quantity of brain.

If we exclude, however, as much as possible, the above mentioned factors which, besides the size of the body, influence the quantity of brain, if we thus compare animals taken in the state of nature, which are as near as possible to one another, systematically, in their manner of life and in the shape of their bodies, but differ as much as possible in the size of their bodies, then it must be possible, to discover at least, if it is not a simple proportion, some relation existing between the quantity or mass of brain and the size, the weight of the body.

About twenty years ago the necessary, trustworthy evidences, chosen and explained with critical discernment, were very rare. Thankfully it may be remembered here that it was MAX WEBER, who, by procuring them, was one of the first that prepared the way for the treatment of this problem, at least in so far as regards Mammals [1]).

At all events the size of the body remains a very important factor amongst those determining the quantity of brain, for the Lion e. g. possesses absolutely 7 times as much brain as the Cat, the Brown Rat 6 times as much as the Mouse. Evidently the weight of the brain is, after all, a (mathematical) function of the weight of the body. If the quantity of brain does not increase proportionally to the volume of the body, expressed by the weight, it might be that this is really the case with regard to the superficial dimensions, as being proportional with the receptive sensitive surfaces and with the sections of the muscles, thus measuring the passive and active relations of the animal to the outer world, for which in this way the quantity of brain can be a measure. Then, in animals equal in organisation and shape, but not in size, the quantities of brain must increase as the $\frac{2}{3}$ power or the power 0.66.. of the weights of the bodies.

In those comparable Vertebrates of different sizes the longitudinal dimension might likewise be the measure of the quantity of

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[1]) Especially in his "Vorstudien über das Hirngewicht der Säugethiere". Festschrift für CARL GEGENBAUR. Leipzig 1896.

brain, on account of the segmental structure, and the movement by the contraction of muscle-fibres, working on levers proportional to the length of the body in this tribe of animals.

Again, the extension or the specification of some definite receptive surface (of sense) may likewise determine the quantity of brain. As the former in its turn must be a (mathematical) function of the size of the bodies of animals that are equal in shape and organisation, it must, according to some (arithmetical) power-proportion of the weight of the body, be one of the factors determining the quantity of brain.

However insolvable, at first sight, the problem indicated by the title of this communication may seem to be — as no organ is more complicated of structure and in its physiology more obscure than the brain — in this way it must be possible to make it fit for solution. It must, at all events, be possible, likewise for groups of animals of different grades of organisation, to represent the *cephalisation* by figures, and thus to compare them.

Be r the required exponent of correlation (indicating the correlation of the brain quantity to the mass of the body), be e (encephalon) the weight of the brain, s (soma) the weight of the body of the smaller animal, E and S the weight of the brain and the weight of the body of the larger animal and k (kephalisation) the coefficient of cephalisation, equal for both, then we have the following equations:

$$E : e = k\,S^r : ks^r$$

$$E : e = S^r : s^r$$

$$\left(\frac{S}{s}\right)^r = \frac{E}{e}$$

$$r = \frac{\log E - \log e}{\log S - \log s}$$

$$k = \frac{E}{S^r} = \frac{e}{s^r}$$

When working these equations by evidences contributed by MAX WEBER and others I found in 1897[1]) at a seven times repeated

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[1]) The proportion of the weight of the brain to the size of the body in Mammals. Verhandelingen der Kon. Akademie van Wetenschappen te Amsterdam. Volume 5. No. 10. Amsterdam 1897.

Also in French and German text: Sur le rapport du poids de l'encéphale avec la grandeur du corps chez les Mammifères. Bulletins de la Société d'Anthropologie de Paris 1897. p. 337 – 376.

Ueber die Abhängigkeit des Hirngewichtes von der Körpergrösse bei den Säugethieren. Archiv für Anthropologie. Band 25. Heft 1 und 2. Braunschweig 1897, p. 1—28.

calculation for each time two Mammals of different orders: Primates, Ruminants, Carnivores, Rodents, always only values varying mutually between 0.54 and 0.58, with an average of 0.56 or about $\frac{5}{9} = 0.55 \ldots$

Arranging according to k calculated in this way, we see indeed the great confusion prevailing in the arrangement of Mammals according to the relative weights of their brains, give place, in a generally satisfactory manner, to an arrangement that is pretty well in conformity with the natural system. A few deviations continue to exist, the Elephant e. g. takes his place between Man and the Anthropoid Apes, the Rodents deviate mutually very strongly. On the other hand the different behaviour of Macrochiropteres and Microchiropteres indicates rightly their different origin.

In 1905 the above-mentioned method of investigation was applied to Birds by LOUIS LAPICQUE and PIERRE GIRARD [1]). By 5 comparisons (Hooded Crow—Jay, Carrion Crow—Jay, Wild Duck—Summer Teal, Silvery Gull—Sea Swallow, Buzzard—Kestrel) they obtained for r a value that was so near the one I found for Mammals, that their conclusion, that for Birds the same exponent of correlation may be accepted, was entirely justified. According to the value of the coefficient of cephalisation calculated by this method, Birds, though not entirely after the natural system, yet with regard to the nearest affined ones, may be classified in a natural way. Parrots, the Monkeys among Birds, stand highest in the list [2]).

Afterwards a few other comparisons (Swan—Summer Teal, Eagle—Kestrel, Parrot—Parrakeet, which species showed greater differences in the sizes of their bodies), could be added by LAPICQUE [3]) to the first 5 comparisons; in this way still better results were obtained. The 5 most thrustworthy comparisons gave now an average $r = \mathbf{0.558}$.

This constant returning of "cette puissance étrange" 0.56, the meaning of which is absolutely incomprehensible according to LAPICQUE [4]), likewise in Birds, where the anatomical composition of the brain is certainly very different from that of Mammals, must indeed be called exceedingly striking.

Under these circumstances it was of great interest to investigate

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[1]) Comptes rendus des séances de l'Académie des Sciences. Paris 1905, 1, Tome 140, p. 1057—1059.

[2]) Bulletins du Muséum d'histoire naturelle. Paris 1909. p. 408—412.

[3]) Revue du Mois. Paris. 10 Avril 1908.

[4]) Revue du Mois. Avril 1908. p. 445. Further: Bulletins et Mémoires de la Société d' Anthropologie de Paris. Séance du 2 Mai 1907. 5me Série, Tome 8, fasc. 3. Paris 1907, p. 261.

the relation between quantity of brain and size of the body likewise for the lower classes of Vertebrates. This is connected here with greater difficulties, for whereas in Birds the relative weight of the brain is still of the same order of amount as in Mammals, it descends in the inferior classes, both absolutely and relatively, as low as to the order of magnitude of about $^1/_{10}$ of that of the two highest classes. The quantities of brain we have to deal with are thus absolutely little, and we can only make use of those rare cases of the usually very scarce evidences about these classes, in which the weights of the bodies show great differences. A few accurate evidences are found in WELCKER's "Gewichtswerthe der Körperorgane bei dem Menschen und den Thieren", published after the author's death by A. BRANDT [1]. Further L. LAPICQUE and H. LAUGIER [2] gave in 1908 some trustworthy determinations of weight, and lately G. WATERLOT, who had made himself conversant with the technical method in the Laboratory of LAPICQUE, published a great number of weights of brains and bodies of Vertebrates, among which also Reptiles and Amphibia, determined in Dahomey [3].

As early as 1855 and 1856 E. CRISP gave trustworthy evidences concerning a Reptile and a Fish [4].

Among WATERLOT's Reptiles were a Monitor and a Gecko, belonging both to the same sub-order of the Lacertilia as likewise the Emerald-Lizard, of which LAUGIER and LAPICQUE communicated the weight.

All were full-grown animals, the Monitor (Varanus niloticus) was a subject of mean size; four individuals of the little Gecko (Hemidactylus Brooki) were weighed and consequently average weights can be calculated. The weight of the body of the Varanus is 1600 times that of the Gecko and almost 450 times that of the Emerald Lizard. Under these circumstances trustworthy results may be expected. A third good comparison of Reptiles affords a Viper (Vipera berus), of which CRISP weighed 7 individuals, with a Cobra (Naja melanoleuca) of Dahomey, weighing almost 28 times as much. A few other Reptiles have been inserted into the following table. The values of k calculated with $r = 0.56$ are likewise indicated in it, as well as the average diameter of the eye-ball of some species [5].

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[1] Archiv für Anthropologie. Vol. 28 (Braunschweig 1902), p.p. 55—61.

[2] Comptes rendus. Soc. de Biologie. Paris 1908, Vol. 64. p. 1108.

[3] Bulletins du Muséum d'Histoire naturelle. Paris 1912, p. 491.

[4] E. CRISP, Proceed. Zool. Soc. London. Part. 23. (1855), p. 191. Ibid. Part 24. (1856), p. 106.

[5] N⁰. *1*, *2* and *4* have been borrowed from WATERLOT (l.c.), *3* and *8* from LAPICQUE (l.c.) *5* from CRISP l.c. (1855), *6*, *7* and *9* from WELCKER—BRANDT (l.c.). — An Alligator mississippiensis from HRDLICKA, cited by LAPICQUE (Bull. et Mém. Soc.

	S	E	k	Average diameter of the eye ball, in m.m.
1. Monitor (Varanus niloticus) (1)	7500. G.	2.440 G.	0.0165	12.5
2. Little Gecko (Hemidactylus Brooki) (4)	4.7	0.043	0.0181	4.1
3. Emerald Lizard (Lacerta viridis) (aver.)	16.8	0.093	0.0191	5.8
4. Cobra (Naja melanoleuca) (1)	1770.0	0.646	0.0098	7.0
5. Common Viper (Vipera berus) (7)	64.2	0.105	0.0102	
6. Common Lizard (Lacerta agilis) (2)	12.507	0.076	0.0185	
7. Slow Worm (Anguis fragilis)	16.252	0.039	0.0082	
8. " " " "	18.9	0.037	0.0071	2.8
9. Greek Tortoise (Testudo graeca)	993.58	0.360	0.0075	

Herewith the following values for r are obtained. By comparison of *1* with *2*: 0.5476, of *1* with *3*: 0.5355, *4* with *5*: 0.5478. The average for the examined Reptiles is **0.5436**.

All these values are again so near to 0.55 . ., or $^5/_9$, that there is no doubt but the same exponent of correlation may be accepted for the three highest classes of Vertebrates. Here already I point to the low value of k both of the Slow Worm (Anguis fragilis) and of the Snakes in contradistinction to the Lizards.

Regarding Amphibia I have not been able to obtain entirely satisfactory data for the calculation of r. The giants among these, as the American Bullfrog (Rana mugiens or Catesbyana) and the Indian Tiger-spotted Frog (Rana tigrina), reach only 5 times the size of the nearest related species to be compared with. For the Bullfrog I have calculated of Donaldson's[1] 6 largest individuals the value of s 244.4 G. and of e 0.204 G. A comparison of the latter with our Waterfrog (Rana esculenta), according to Lapicque's averages for s and e, gives only an exponent of correlation of 0.3843. Compared with Lapicque's Rana fusca (aver.) r becomes on the contrary $=$ **0.5501**. It seems that the Bullfrog, at least in the organisation of the nervous system,

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d'Anthrop. l. c. p. 263), with $s = 11.34$ KGM affords, as not full-grown, probably too high a k (0.0268). For a "Crocodile" mentioned by Manouvrier ("Sur l'interprétation de la quantité dans l'encéphale". Mémoires de la Société d'Anthropologie. Paris 1885. 2me Série, Tome 3, 2me fasc. p. 167) of about 70 KGM body weight, we find $k = 0.0290$.

[1] Decennial Publications. University of Chicago. Vol. X. (1902), p. 7 and Journal of Comparative Neurology. Vol. 8 (1898), p. 330.

is more closely allied with the European Landfrog than with the Waterfrog. The similarity in the modus of living with the latter has no influence in this respect. The following calculations of k for some Amphibia prove indeed that other factors are predominant there.

Valuable evidence for the calculation of the exponent of correlation for this class might be obtained from the Japanese or the American Gigantic Salamander (Megalobatrachus maximus and Cryptobranchus Alleghaniensis). The former is certainly more than 100 times heavier than the Spotted Landsalamander, and surpasses the Crested or Great Newt more than 400 times in weight. But, as far as I know, this evidence does not exist.

If we admit for Amphibia the same exponent of correlation as for the three highest classes of Vertebrates, then we find the following values for k.

	S	E	k
1. Waterfrog (Rana esculenta) (aver.)	44.5 G.	0.106 G.	0.0127
2. Leopard Frog (Rana virescens) (5)	73.35	0.153	0.0138
3. Bullfrog (Rana Catesbyana) (6)	244.4	0.204	0.0094
4. Landfrog (Rana fusca) (aver.)	53.0	0.088	0.0095
5. Common Toad (Bufo vulgaris) (aver.)	44.5	0.073	0.0087
6. Shackletoad (Alytes obstetricans) (aver.)	7.7	0.041	0.0131
7. Treefrog (Hyla arborea) (aver.)	4.8	0.043	0.0179
8. Spotted Landsalamander (Salamandra maculosa) (1)	24.88	0.047	0.0078
9. Great Water-Newt (Triton cristatus) (2) ¹)	7.46	0.019	0.0062

The comparatively high value of k in the two first mentioned species, likewise in Alytes obstetricans and especially in the Treefrog, has evidently some relation with a higher organisation of the nervous system, and not with the surroundings in which the animals live. Rana Catesbyana lives, as likewise R. esculenta and R. virescens, in water, ranks however near to R. fusca, the Landfrog. The deviation of k in this respect is in the latter analogous with

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¹) N'. *1, 4, 5, 6, 7* are borrowed from Lapicque and Laugier (l.c.); *2* and *3* from Donaldson (Journal of Comparative Neurology. Vol. 10. (1900), p. 121 [the 5 largest Rana virescens (♀)], Journal of Comparative Neurology. Vol. 8. (1898), p. 330. Decennial Publications. Chicago. Vol. 10. (1902), p. 7 [the 6 largest Rana Catesbyana]; *8* and *9* from Welcker-Brandt (l.c., p. 57 and 58).

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that of Salamanders and Newts, where the latter, which live in water, have however lower cephalisation than the Landsalamander. In general the value of k does not differ much from that of Reptiles.

If now we find in the lowest class of Vertebrates, the Fishes, for r the same value as for the three highest classes, then it is certain that also in the Amphibia, which rank between them, the same relation exists between weight of the body and weight of the brain.

Of the following evidence regarding Fishes the greater part has been borrowed from Welcker-Brandt [1]).

	S	E	k
1. Carp (Cyprinus carpio)	1817.3 G.	1.270 G.	0.0190
2. Crucian (Carassius vulgaris)	5.22	0.470	0.0186
3. Gudgeon (2) (Gobio fluviatilis)	42.196	0.159	0.0195
4. Perch (Perca fluviatilis)	67.27	0.162	0.0153
5. Stickleback (2) (Gasterosteus aculeatus)	1.447	0.022	0.0179
6. Pike (Esox lucius) [2])	12700	4.860	0.0245
7. Conger (Conger vulgaris) [3])	10000	1.050	0.0060
8. Eel (Anguilla Anguilla) [3])	650	0.170	0.0045

When comparing each time two, the nearest affined species, the following values for r are found: *1* with *2*: 0.5633, *1* with *3*: 0.5522, *4* with *5*: 0.5201, *6* with *2*: 0.5949, *7* with *8*: 0.6661.

With the exception of the last, to which I shall revert afterwards, these values are also all near to 0.55 . . . The average of the four is **0.5576**.

Eels (Muraenidae) excepted, the comparatively high values of k, in which most Fishes equal even the examined Reptiles, are striking. In the low value of k in the Eels we find a similar phenomenon, the probable cause of which I shall indicate afterwards, as

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[1]) L. c., p. 59–61. There 3 more perches. The statements for them deviate however so much from what may be admitted as normal for this species, that they cannot be used separately for trustworthy calculation of r. Compared with the 2 sticklebacks they give for r values ranging from 0.437 to 0.644. The average of 4 comparisons is 0.525.

[2]) E. Crisp in Proceed. Zool. Soc. London. Part. 24. (1856), p. 106.

[3]) L. Lapicque, Bull. et Mém. Soc. d'Anthrop., l.c. p. 263.

in the Snakes and the snake-shaped Slow Worm, but the deviation is here still greater on account of a second cause.

The results obtained in this way seem to prove with certainty the existence of a law that can be applied to all Vertebrates, indicating the relation between quantity of brain and size of body.

In species of Vertebrates that are equal in organisation (systematically), in their modus of living and in shape, the weights of the brains are proportional to the $^5/_9$ power of the weights of the bodies.

Before we try to discover the meaning of this law, it is important to determine the value of the exponent of correlation for the brainweight of large and small individuals in one and the same species. The differences of size of the body are, in most cases, comparatively much less here than those between the species mutually, and we are generally obliged to take averages of a great number of individuals, to make the errors attending each special observation balance as much as possible against one another. With the exception of such species as the Dog, having many races of very different sizes, the best evidences can consequently be found for Man.

The result I obtained in this respect for Man, in 1898, was completely contradictory to what I found for different species of Mammals.[1]) The exponent of correlation proved to be an entirely different one. For obvious reasons we cannot dispose, with regard to Man, for this calculation of sufficient evidence, relating to normal weights of the body belonging individually to the weights of the brain. In order to be able to compare these quantities, we may follow two indirect ways. In the first place it is possible to *calculate* the weight of the brain of living Man. According to the method of WELCKER, which has proved to be very trustworthy, I calculated the weights of the brains of four groups, each of 10 strong, healthy, and not fat young men, from the dimensions and shapes of their heads, which evidences OTTO AMMON had been kind enough to provide me with. It had been ascertained for those 40 men that they did not grow any more. They were all small farmers and day-labourers from Baden. In this way I found an exponent of correlation of about 0.25, the value **0.245** (of two of the six combinations possible) is probably more correct.

Taking the second way I calculated r from the *directly determined* weights of the brains of Englishmen (Londoners) with average weights of bodies of men of the same social class, according to the

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[1]) Ueber die Abhängigkeit des Hirngewichtes von der Körpergrösse beim Menschen. Archiv für Anthropologie. 4°. Bd 25. Heft 4. Braunschweig 1898, p. 423—441.

unsurpassed data of JOHN MARSHALL[1]). Here the value of **0.219** was found for *r*.

I tried to explain that strongly deviating behaviour of individuals of Man, differing in size, in comparison with species of Mammals of different sizes, by the uncomparatively great supremacy of the brain over other organs and parts of the skull in Man. The inferior augmentation of the brain with the size of the body might be a consequence, in my opinion then, of an exceptionally strong progressing folding of the grey cortex, going hand in hand with that augmentation of the brain as a whole. At the present state of our knowledge, now that we know that in all Vertebrates in general, independently of its shape and structure, the augmentation of the brain is equal for all species that are of a similar organisation, the interpretation then given, that can only be applied to Man, must be entirely abandoned. I should certainly immediately have rejected it, if I had known that, a few months previously in 1898, LAPICQUE, when applying the relation I had found for Mammals, to dogs of different sizes, according to evidences borrowed from a series of RICHET, had obtained the same result, as I now found for Man. That result had, moreover, only been communicated by LAPICQUE in a report of the proceedings of the meeting of the Société de Biologie on the 15th of January 1898, in hardly a single page of printing[2]) together with the announcement of my memoir on Mammals.

His conclusion ran: "Tout ce que je veux établir aujourd'hui, c'est que la puissance de P (the weight of the body), suivant laquelle varie l'encéphale d'espèce à espèce étant 0.55, dans l'espèce chien cette puissance est 0.25, c'est à dire extrêmement différent". Simultaneously with my paper on Man of 1898, in the "Archiv für Anthropologie", LAPICQUE published with DHÉRÉ another article[3]), in which the authors communicate as briefly the result for the Dog, mentioned above, and, on account of an examination of the chemical composition of the brain, try to find an explanation of the exponent found for this species in the relative amount of white and grey

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[1]) On the relations between the weight of the brain and its parts, and the stature and mass of the body. Journal of Anatomy and Physiology. Vol 26. London 1892. p. 445. There the weights of the bodies of living men, according to JOHN BEDDOE (Memoirs. Anthrop. Soc. London. Vol. III. 1870, p. 533).

[2]) "Sur la relation du poids de l'encéphale au poids du corps" in "Comptes rendus hebdomadaires des séances de la Société de Biologie". Paris 1898. N⁰. 2 (21 janvier 1898), p. 63.

[3]) "Sur le rapport entre la grandeur du corps et le développement de l'encéphale". In "Archives de Physiologie normale et pathologique", N⁰. 4. Octobre 1898. Paris. p. 763—773.

substance varying with the size. They ask themselves the question, if the law found for the Dog may in general also be applied to other species, and give a negative answer to it. "*A priori*, on doit estimer que non, et nous avons soin de dire que notre étude porte sur un cas particulier." (p. 765). In conclusion they say: "Il y a donc, en passant des petits aux grands chiens, une différence sensible de la composition chimique, et, par suite, l'unité de poids ne représente pas pour les uns et pour les autres des valeurs physiologiques identiques", (p. 773).

It is clear, that by LAPICQUE and by me, independently of each other and unprejudiced, an identical result has been obtained for two very different species of Mammals. If this circumstance increases considerably the importance of this result, then it appears at the same time that neither of us surmised he had found an interindividual exponent of correlation equal for all species.

Calculating the value of r for the dog found by LAPICQUE, proportional to the number of observations used for each comparison, afterwards[1]) communicated by him, I find it to be $= 0.235$. When he repeated the investigation applied to Man, which had caused me to find the two above mentioned values of r 0.245 and 0.219, with other evidences, according to the second method, he found for Man 0.23 and for Woman 0.224. A comparison of the averages of 7 larger with 7 smaller individuals of an American Squirrel (Sciurus carolinensis), which 14 individuals with a smaller American species (Sciurus carolinensis) (6 individuals) had furnished an exponent of correlation of 0.56, gave an interindividual exponent of 0.20[2]). With two groups of 5 female Moles of MANOUVRIER I find 0.234[3]). The average of these seven observations is **0,228**.

A number of other comparisons, with less good evidences, however, constantly furnished values that do not differ much from the average found in this way. When I compare the above-mentioned weights of the six largest Bullfrogs of DONALDSON (l. c.) with the six next in size of the same species, I find an exponent of correlation of 0,2516.

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[1]) "Le poids encéphalique en fonction du poids corporel entre individus d'une même espèce". Bulletin et Mémoires de la Société d'Anthropologie de Paris. Séance du 6 juin 1907. 5me Série, Tome 8, fasc. 4. Paris 1908, p. 315.

[2]) LAPICQUE, "Le poids encéphalique en fonction du poids corporel entre individus d'une même espèce", l. c. p. 327.

[3]) There must be errors in MANOUVRIER's statements (Mémoires Soc. d'Anthrop. Paris 1885, p. 213 and p. 297) concerning two groups, each of 7,♂ moles, as the heavy individuals should on an average only possess 1 m.g. more brain than the lighter ones; the average likewise points to these errors. Consequently these groups are useless for the calculation of the interindividual r.

Taking into consideration that the certainly still more correct lines of Donaldson[1]) give to r a value of 0.2316, we may call this result very satisfactory. On grounds to be discussed afterwards we may admit that indeed *the exponent of correlation within the same species of all Vertebrates* is **0,22**. . .

In my previous communication of the result for Mammals I had borrowed, on behalf of a provisional comparison with Man, for the calculation of k available evidences from the 2nd edition (of 1893) of Vierordt's "Daten und Tabellen". Calculating with the general exponent of correlation 0,56 I found then a somewhat different value of k for Man and for Woman. If I had made use of more accurate evidences, the cephalisation would have been found identical for the two sexes, as has indeed been proved by Lapicque[2]) in 1907, and at the same time it would have been proved that between Man and Woman of different size the same exponent of correlation obtains as between species that are equivalent with regard to the organisation of the nervous system, but differ in the size of the body.

I can now affirm this by two more series of evidences. Placing namely the four groups of English men of average size, borrowed from Marshall, used for my calculation of the exponent of correlation for Man, beside the four groups of average English women of his Table XVIII (l.c., p. 498) we find 63685 G. and 54432 G. for the average weight of the bodies and 1353.7 G. and 1233.2 G. for the average weight of the brain. The result of the calculation is $r = 0,594$.

For the average weights of the brain of English and Scottish men and women we obtain 1375 G. and 1235 G., according to seven different observers, cited in the new edition of Vierordt's "Daten und Tabellen".[3]) The weights of the body for full-grown men and women of that nationality, according to Roberts, cited there, are 63010 G. and 52170 G. (deduction made for what Roberts indicates for the weight of the clothes). With this value r can be calculated at 0,568.

Calculating with the weights of the body according to Roberts and the weights of the brain according to Marshall we find 0,498. The average of these three results is **0.553**.

There are no sufficient evidences at hand for testing this sexual difference in species of animals. Kohlbrugge[4]) gives the weights of

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[1]) For these comparisons E and e were borrowed from the graphical representation in Donaldson's publication of 1898 (l. c. p. 322).

[2]) "Le poids encephalique en fonction du poids corporel entre individus d'une même espèce". l. c. p. 344.

[3]) Dritte Aufl. Jena 1906, p. 23—24, 75—76.

[4]) Zeitschr. f. Anatomie und Morphologie. Bd. II (1900), p. 51—55.

the body of the Javanese Budeng (Semnopithecus maurus and pyrrhus) relating to 11 female and 7 male individuals and the weights of the brain of 4 female and 3 male individuals. It is a great pity that a few errors must have slipped into these precious statements of the weights of the bodies [1]. It is, however, possible to calculate 0.553 or 0.586 for the intersexual exponent of correlation, either when correcting the presumable errors or when omitting these erronical weights of the body.

What has been stated for Man, considered in connection with the rational meaning of the exponent of correlation 0.55 still to be discussed, gives us already a right to admit that for Vertebrates in general the following law exists: *The sexes differing in size of one species are in the quantity of brain proportional to each other as two different species with identical organisation of the nervous system.*

The attention may here be called to the fact that this law is in accordance with the result of the latest investigations about the hereditary transmission of sex [2], as with those of DUMBAR on the sero-biological behaviour of the sexes in plants and animals.

Further I want to point out that there is a connection between the relation of the two sexes found and the non-existence of the disproportion in the relative length and thickness of the bones, which is so striking a feature between the large and the small individuals of one species. [3] Both sexes behave, in this respect too, as nearly related species of very different sizes.

[4] The uniformity of the correlation found between quantity of brain and size of body in all classes of Vertebrates, however striking, cannot, properly, surprise us, as we did eliminate a priori all other important influences on the quantity of the brain, save *the size of the body.* That uniformity affords proof that indeed we succeeded in eliminating those other influences and, moreover, that the size of the body influences the quantity of the brain in the same way in all classes.

One may, however, consider it strange that the well known increase of the relative amount of white substance (composed chiefly of medullated fibres) contrary to the grey substance (containing the

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[1] It seems indeed that in three cases pounds are written erroneously for kilos.

[2] C. CORRENS and A. GOLDSMIDT, Die Vererbung und Bestimmung des Geschlechtes. Berlin 1913.

[3] Species with a relatively slight difference of size (as e.g. Hylobates syndactylus and H. leuciscus) show a disproportion in a reverted sense: between species of very different size this is scarcely perceptible.

[4] The passage between brackets is added in the English translation.

bodies of nerve cells), an increase going on, systematically, with increasing quantity of the entire brain, does not appreciably corrupt those results.

It was this consideration that induced Dhéré and Lapicque to investigate the chemical composition of the brain in large and small dogs. 1) From their results it is obvious that the real disproportion between the two constituents in large and small brains of nearly related animals, though existing, is insignificant when compared with what it seems to be on sections of those brains and from superficial mathematical reflection. We may infer that the seemingly very striking disproportion is, to a very large amount, corrected by other variations going hand in hand with augmentation of the quantity of brain, namely increasing thickness and folding of the cortex and less rounded form (i.e. relatively more extended surfaces) of the larger brain, these three processes (or two in the brains without folding) tending to increase the relative amount of grey substance.

The positive knowledge, obtained in this way, of the relation between quantity of brain and size of the body, in species and individuals, gives now a meaning to that "puissance étrange" 0.55.. and at the same time 0.22.. by which those relations are determined.

Referring to the arguments in my memoir of 1897 on the peculiar relation of the eye to the size of the body, and continuing the analysis of the exponent 0.56 or 0.55.., I believe that it will be easy to prove its rational character, as well as that of the exponent 0.22 .. In this way the correlations we found are raised to the rank of real biological laws.

In the memoir of 1897 I had already pointed out that the factor that expresses the deviation from the simple relation between weight of the brain and superficial dimension of the body is the cube-root of the linear dimension of the body.

$S^{0.55\ldots}$ can be analysed as follows:

$$A.\quad S^{0.66-0.11} = S^{\frac{2}{3}-\frac{1}{9}} = \frac{L^2}{L^{\frac{1}{3}}} \qquad\qquad B.\quad S^{0.22+0.33} = S^{\frac{2}{9}+\frac{3}{9}} = L^{\frac{2}{3}} \times L$$

The relations found above can then be described as follows:

I. In species of Vertebrates that are alike in the organisation

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1) "Sur le rapport entre la grandeur du corps et la développement de l'encéphole." l.c. (1898).

of their nervous system and their shape, but differ in size, and also in the two sexes of one and the same species, the quantity of brain increases:

A. as the quotient of the superficial dimension and the cube-root of the longitudinal dimension.

B. as the product of the longitudinal dimension and the square of its cube-root.

II. In individuals of one and the same species and of the same sex, differing in size, the quantity of brain increases as the square of the cube-root of the longitudinal dimension of the body.

Consequently we find between the exponents 0.22.. and 0.55.. a relation of a simple nature.

Moreover the factor $S^{0.22}$ or $L^{\frac{2}{3}}$ in *B* is the square of the denominator in *A*.

The fact that, in different species, a factor determining the quantity of brain is to be found in the superficial dimension of the body, which is the measure of the sensitive surfaces as well as of the muscular force, was discussed at large in my memoir of 1897. It is neither incomprehensible, that individuals of different size in one and the same species distinguish themselves from, for the rest closely resembling species differing in size, because only in the latter case an increase of the quantity of brain proportional to the longitudinal dimension takes place, as a consequence of segmental growth, increase of sensu-motorical unities in segmentically constituted species of animals.

From the investigations of I. **Hardesty**[1]) it appears that in the Elephant, which is 180000 times heavier than the Mouse, and in Man, who is 3628 times heavier than the Mouse, the masses of certain nerve-cells of the spinal-cord are proportional as the imaginary longitudinal dimensions of the mentioned species.

If we admit that to every nerve-fibre a definite central cell-mass answers, then these masses must increase with the number of nerve-fibres, in segmentically constituted animals indeed as the longitudinal dimension.

But what is then the meaning of $L^{\frac{1}{3}}$?

The answer to this question was likewise prepared in my memoir of 1897. It is to be found in the very special relation between the size of the eye and the body in animals of different sizes. The longitudinal dimensions of the body and the eye of these animals

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[1]) Journal of Comparative Neurology. Vol. 12 (1902), p. 125—182.

are not proportional to each other, neither are they absolutely equal; in other terms, the smaller animal has, in proportion to its body, a large eye, yet it is absolutely surpassed by that of the larger animal. We find here evidently a similar relation as between the weight of the brain and that of the body, and can try to fix this relation in a similar way, by calculating an exponent of correlation.

Most fit for this comparative investigation are again species that differ as much as possible in size, and have at the same time absolutely large eyes. Instead of the simple diameter of the eye-ball (which in its shape and in the thickness of the sclerotica is variable) it is preferable to compare the linear sizes of the images on the retina. More than twenty years ago Matthiessen[1]) made exact measurements of the sizes of the images on the retina, amongst others in Whales, which together with others were already formerly discussed by me. He does not indeed indicate the sizes of the animals themselves, but if we admit for them the averages of the full grown species, then the error resulting from this insufficient information cannot be very great.

Let us thus compare the largest of the four examined species of Whalebone-Whales, Sibbald's Fin-Whale, with the smallest, the Humpback Whale, and calculate according to what exponent of correlation of the length of the body proportionality with the size of the image is obtained[2]).

	Proportion of	
	linear sizes of the images (in Millimeters)	lengths of the body (l) (in Meters)
Larger Fin-Whale (Balaenoptera Sibbaldi) and Humpback-Whale (Megaptera Boops)	$\frac{39.78}{30.23}$	$\frac{30}{15}$

We find then that on an average the lengths of the body must be involved to the power 0.3964 to become proportional to the lengths

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[1]) L. Matthiessen. Die neueren Fortschritte unserer Kentnis von dem optischen Baue des Auges der Wirbelthiere. Festschrift für H. von Helmholtz 1891, p. 62-63.

[2]) The Porpoise (mentioned by Matthiessen as "Delphinus communis") and the Whalebone-Whales belong to phylogenetically different orders, Ondontocetes and Mysticetes, which differ greatly both in the relative size of the eye and in the cphalisation (this in reverted proportion). Therefore they cannot be compared here.

of the images, i.e. *almost* $\sqrt[3]{l}$ or $\sqrt[9]{S} = S^{0.111}$, correctly $S^{0.132}$ or $\sqrt[7.6]{S}$.

In the interesting essay of AUGUST PÜTTER[1]) I find, in text and in figures, statements both of the retina-surface and of the size of the body of full-grown individuals of Hyperoodon rostratus, the Bottlenose-Whale, and of Phocaena communis, the Porpoise, both Odontocetes. The lengths of the bodies are proportional as 6 : 1, and the diameters of the retina as 2 : 1. From this follows, that those diameters increase as $\left(\frac{S}{s}\right)^{0.133\,..} = \sqrt[7.5]{\frac{S}{s}}$.

In my memoir of 1897 a Lion was also compared with a Cat for the calculation of the exponent of correlation. The exponent of correlation I found was 0.5466. The coefficient of cephalisation, calculated with 0.55 . ., gives therefore a different result for them. In order to obtain equality, the S of the Lion must only be a little diminished (according to the proportion that presumably existed between the two individuals examined by MATTHIESSEN). Then the proportion of lengths of the images in the eyes, measured for both species, $= \frac{18.95}{11.80}$, is exactly equal to $\sqrt[7.5]{\frac{S}{s}}$.

An equal relation is found between the Sea-eagle and the Hawk.

The general validity of this relation is especially obvious when comparing little animals with enormously large ones. The shapes of the bodies can then even be greatly different, if only there is no great deviation in the coefficient of cephalisation. Among the animals of which MATTHIESSEN has measured the lengths of the images, are also the Fox, the Cat and the Rabbit. The weights of the bodies of these animals and also of that of Sibbald's Fin-Whale, (of which several individuals have been examined) are approximately known.

Between these the following relations are found:

	$\left(\frac{S}{s}\right)^{0.133}$ in Kilograms	Proportion of the lengths of the images (in Millim.)
Sibbald's Fin-Whale and Fox	$\left(\frac{100000}{6}\right)^{0.133} = 3.643$	$\frac{39.78}{9.42} = 4.223$
" " " Cat	$\left(\frac{100000}{3}\right)^{0.133} = 3.995$	$\frac{39.78}{11.80} = 3.371$
" " " Rabbit	$\left(\frac{100000}{1.5}\right)^{0.133} = 4.381$	$\frac{39.78}{9.19} = 4.329$
Average	— 4.006	— 3.974

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[1]) Zoologische Jahrbücher. Abtheilung für Anatomie und Ontogenie der Thiere. Jena 1903. p. 240, 243, 273 and 280.

LAPICQUE has measured the diameters of the eyeballs of a number of Vertebrates and found for Mammals an exponent of correlation first of $\frac{1}{8}$, afterwards of $\frac{1}{7}$ [1]). For the examined Mammals the measurement of the diameter of the eye-ball was generally sufficient in order to ascertain the size of the retina. He concludes then, as was to be expected from what could be shown already in 1897, that in most cases the size of the eye runs parallel with the weight of the brain.

Those meritorious measurements of the eye-ball by LAPICQUE thus furnish a welcome affirmation of the results obtained here with regard to the images on the retina. We may admit that the linear dimensions of the images vary as $\sqrt[7.5]{S}$ or $S^{0.133\cdot\cdot}$.

If the result had been $\sqrt[9]{S}$ or $S^{0.111\cdot\cdot} = L^{\frac{1}{3}}$, then we should have here the same factor as in the coefficients for the brain, and we should immediately be convinced of its rational character. Now it can, again, not be by chance only that even in apparently absurd comparisons (as those of Sibbald's Fin-Whale with species of little land-animals) that same exponent $^1/_{7.5}$ constantly returns. What is the meaning of this fact?

The answer to this question too is not difficult, for $9 : 7.5 = 0.66\ldots : 0.55\ldots$ If now we consider that, in accordance with the augmentation of the brain with the size of the species of animal, the sensitive surfaces must increase in the same proportion to the superficial dimension of the body, then it becomes comprehensible that the receptive sense-elements in the retina do not remain entirely equally thick with the larger animal as with the smaller one, but become thicker and less closely placed [2]), *in the same proportion.* For this reason the *number* of the nerve-elements in the retina increases only linearly as $\sqrt[9]{S}$ or $L^{\frac{1}{3}}$, in the superficial dimension as $\sqrt[9]{S^2} = S^{\frac{2}{9}}$ or $S^{0.22\cdot\cdot} = L^{\frac{2}{3}}$.

In this way a connection has been established between the exponent of correlation for the eye and the exponent of correlation for

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[1] "La grandeur relative de l'oeil et l'appréciation du poids encéphalique". Comptes rendus de l'Académie des Sciences. Paris, Tome 147, (1908), 2, p. 209. "Relation du poids encéphalique à la surface rétinienne dans quelques ordres de Mammifères". Ibid. Tome 151, (1910), 2, p. 1393. On lower Vertebrates: L. LAPICQUE et H. LAUGIER in Comptes rendus de la Société de Biologie. Tome 64, (1908), p. 1108.

[2] Compare the data in A. PÜTTER, Organologie des Auges. 2nd Ed. Leipzig 1912.

the brain with the mass of the body, within one species, as well as from species to species.

Still it remains, however, an open question why the lengths of the images, as measured by the number of sense-elements, increase exactly as $L^{\frac{1}{3}} = L^{0.33\ldots}$.

In order to find an answer to it, we must consider, that the eye distinguishes itself from the other senses by giving at a distance a representation of the exact place of the energy-source that acts as a stimulus. Consequently it orientates about the direction from which that stimulus comes. Object and image, that is the place of the stimulated sense-elements, answer to each other.

Under these circumstances the distance to the objects must exactly stand in the mentioned relation to the linear dimension of the body. Indeed the receptive nerve-elements of the retina placed in the linear dimension of the image, increase then numerically in the proportion of $L^{0.33\ldots}$ in the larger animal, *their mass* in the linear dimension as L, their mass for the surface of the image as L^2. But that mass determines the amount of the transition of energy that is connected with the stimulation of the sense-elements.

It appears now that the long since known intimate connection of the organ of vision, as exquisite sense of room finding its principal function in governing the movements, can be expressed in a definite measure[1]). As in the movements of animals, differing in the size of their bodies, the mass that is to be removed, increases in the proportion of L^3, the muscle-power however only as L^2, an L-fold sensu-motorical stimulation is required for it. And as all senses are more or less, as the optical sense is absolutely, organs of room, their receptive elements must, in the aggregate, increase in mass in that proportion of L, that is in linear dimension as $L^{\frac{1}{3}}$ in superficial dimension as $L^{\frac{2}{3}}$, or $S^{\frac{2}{9}}$. But the nerve-fibres, the peripherical extremities of which are connected with sense-elements in the retina and also in all other sensitive surfaces, and the corresponding cell masses in the brain must increase as $\sqrt[9]{S^2} = S^{\frac{2}{9}} = S^{0.22\ldots}$.

The denominator of the coefficient $\dfrac{L^2}{L^{\frac{1}{3}}}$ can thus be explained as a relative reduction of the brain of the larger animal proportional

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[1]) In a striking way this connection is demonstrated by **Pütter** (l. c. p.p. 85 et seq. and p.p. 402 et seq.).

to the relative reduction of the sizes of its images, a diminution of the distance from the objects of his sphere of feeling and acting and a diminution of the rapidity of movement in proportion to the lengths of the bodies.

The conclusions we have thus obtained give an explanation of a number of otherwise incomprehensible deviations in the value of the coefficient of cephalisation.

For Bats I calculated in 1897 a (mutual) exponent of correlation of 0.66... It appears that it can be applied both to Macro- and to Microchiropteres. A very large insectivorous Bat from Dahomey (Scotophilus gigas) supplies a welcome control and affirmation of my former results. In Bats the influence of the eye is almost entirely excluded. The senses of touch and hearing determine the quantity of brain and the factor $S^{0.11}$ or $L^{\frac{1}{3}}$ disappears. Calculated with their own exponent of correlation the coefficient of cephalisation still diminishes for the two phylogenetically different groups, of which the Microchiropteres are lowest.

Rodents deviate mutually considerably in the values of their cephalisation. This cannot be explained, as Lapicque surmises, by different size of the eye, though it may play in some cases an inferior part. It is the other senses especially, which, by taking the lead in the nervous life of the animal, determine here the quantity of brain. According to numerous evidences the cephalisation of the Brown Rat and the Black Rat and likewise that of the Housemouse is half that of Hares (and Rabbits) and only a third part of that of Squirrels. In the Hares the sense of hearing, in the Squirrels, the Desert Jerboa (Dipus) and the Garden Dormouse (Eliomys) especially the organ of touch, on account of its high specification (in the hand), has caused the increase of the brain.

The value of k falling very low in Shrews, is trebled with the affined East-Indian Tupaja, which lives like the Squirrel.

Canides have about twice as high a cephalisation as Mustelides, on account of the greater development of their senses of hearing and of smell. Among the last-mentioned family, Otters are hand-animals, and, for that reason, they surpass very considerably the other Mustelides in their cephalisation. They reach the rank of Canides.

The Elephant surpasses the other Hoofed Mammals three times in cephalisation. He ranks even much higher than the Anthropoid Apes. He owes this to his trunk, which has become a prehensile and touch hand, with high "specific energies", and possesses the same combination with a chemical organ (here of smell) as the feelers of Ants.

Some of the American Monkeys (Ateles), which are higher cephalised than the Monkeys of the Old World, *not excepted the Anthropoid Apes,* obtained a third prehensile and touch hand in their tail.

Man certainly likewise owes his high rank to his hand; his cephalisation is almost equal to nearly four times that of Anthropoid Apes, consequently he has risen still higher above the latter, than the Squirrel above the Rat, or the Elephant above the other Hoofed Mammals.

Even in the Amphibia we see the cephalisation of the Treefrog, which uses its fore-feet as hands, increasing considerably.

Among Birds, Owls have a high cephalisation, not so much on account of their large night-eyes, which cause only an enlargement of the images on the retina (in comparison with the Day-Birds of Prey), without augmentation of central nerve-cell mass, but on account of the extremely developed sense of touch in the skin and their very quick ear. The touch-corpuscles at the base of the feathers are incredibly numerous. [1])

The Parrots owe the high value of their k to their handlike paw and pincerlike beak.

In all these cases greater influence of the factor $S^{0.33..}$ by specification of the organ of touch occurs.

The comparatively high cephalisation of Sea-Mammals, usually represented exaggerately (as few full-grown animals have been examined), and that of the Hippotamus, however low in the general organisation of the nervous system, can now easily be explained.

According to the evidence now available, the coefficient of cephalisation of Seals can be computed at 0.6, that of Toothed Whales (Odontocetes) at 0.7 and that of Whalebone Whales (Mysticetes) at 0.4. Seals owe their high cephalisation certainly *partly* to the specifically high development of their sense of touch. But Odontocetes, whose cephalisation is equal to that of Anthropoid Apes, lack certainly a similar high development of the organ of touch. They distinguish themselves from the plankton-eating Whalebone Whales by seeking their subsistence at usually greater depth, even to where perfect darkness prevails. In connection with this fact their eye is smaller than that of Mysticetes, but they possess a still more developed sense of hearing than the latter; in the quiet water of the great deep this organ can function perfectly as a sense of room. In all these Water-Mammals, but mostly in the Odontocetes amongst them, the ear is the most important organ [2]). It is doubtless the crepuscular

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[1]) E. Küster, Morphol. Jahrb. Bd. 34. (1905), p. 126.

[2]) G. Boenninghaus. Das Ohr des Zahnwales. Zoologische Jahrbücher. Bd. 19 1904). p. 338—339. — Compare O. Abel, Palaeobiologie. Stuttgart 1912, p. 458.

light prevailing in the water that makes other senses than the optical one predominate in these Mammals, as likewise in the Fishes, and probably in the Crocodiles (hearing very quick), in comparison with Amphibia and most Reptiles. In the Fishes also the olfactory organ and especially the sense-lines are predominant. This has caused augmentation of the quantity of brain, because the surfaces of the mentioned predominating organs of sense (in opposition to the eye, which forms definite images) increase simply proportional to the superficial dimension of the animal (consequently with the exponent of correlation 0.66...). So in these animals a very considerable increase of the quantity of brain does not signify a high degree of organisation. Calculated by means of the exponent of correlation 0.66...) k becomes for Whalebone-Whales 0.07. for Toothed Whales 0.20 and for Seals 0.18.

In the Snakes and the Slow Worm and likewise in the Eels, on the contrary, the great length of the body is the cause of the low value of k, though this does not therefore indicate an inferior degree of organisation. In proportion to the weight of the body the not specialised segmental sensu-motorical unities are too equivalent for a representation in the brain, proportional to that of other Reptiles and Fishes. The body becomes thereby, as it were, to a certain amount, a ballast for the brain. This is in a more literal sense the case in the Tortoises. In the shell-bearing Vertebrates and also in the elongated animals the influence of the factor $S^{0.33}$ in the analysis B has thus diminished. In the Eels a second cause of diminution of the quantity of brain exists *moreover*, in their life as animals of darkness, by the disappearance for the greater part of the eye-factor $S^{0.22}$ in the analysis B and at the same time of the eye-factor in the analysis A (as in the Bats). On account of the latter circumstance their r becomes $= 0.66$.

The influence of the not segmentally constituted eye *in itself* remains in all cases restricted, from the nature of the factor $S^{0.22}$ which depends on it, and is thus less capable of increase. Even the Horse, which possesses an absolutely larger (day-) eye than the Elephant, rises still little above the average level of k for Mammals. On the other hand can the other factor $S^{0.33}$, the segmental factor in analysis B, grow, as it were, endlessly with the development of "specific sense-energies" in the different segments. The tactile organs have therefore always the lead with the higher organisation of the nervous system.

25 November 1913.

Physics. — *"On the question whether at the absolute zero entropy changes on mixing."* By Dr. W. H. KEESOM. Supplement N°. 33 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. The formula for the entropy of the "gramme-molecule" of a mixture of ideal, not reacting gases, for each of which $pV=RT$ is valid, contains the expression

$$-R\,\Sigma\, c_1 \ln c_1 , \quad \ldots\ldots\ldots \quad (1)$$

if c_1 represents the number of gramme-molecules of the first component, c_2 that of the second component etc., which are present in the gramme-molecule of the mixture. Σ will indicate in this paper a summation over the different components.

The expression (1) passes unchanged into the formula for the entropy of the mixture, when this is transferred from an ideal gas condition as considered above into other conditions.

According to PLANCK's version of the NERNST heat theorem the entropy of a one-component substance in a condensed state approaches to a finite value, which is independent of the pressure and of the special state of aggregation, when the absolute temperature approaches to 0. That value may be taken as a suitable zero point for the entropy of that substance in the condensed state.

As it is not immediately evident, how the other terms which occur in the expression for the entropy of a mixture, can on approaching to $T=0$ furnish a compensation of the term written above, it might be imagined, that for a mixture on approaching to $T=0$ the entropy might not become 0, notwithstanding this is the case for the components.

In that case, however, at a temperature which differs little from the absolute zero, any reversible isothermal change of the components, in a condensed state, individually would be connected with a development or absorption of heat, which approaches more rapidly to 0 than the temperature. The reversible mixing of those components, on the other hand, would be accompanied by a heat-effect, which approaches to 0 as rapidly as (eventually more slowly than) the temperature. In other words the mixing heat would be of a different order of magnitude from the heat of each reversible isothermal process performed with the components individually.

It seems to me that it is more natural to assume, that *also for a mixture the entropy at the absolute zero point is equal to* 0, if this is the case for the components by the choice of this point as a zero point for the corresponding entropies.

Probably even the compensation referred to above already takes place in the ideal gas state, at least if the volume of the mixture is not increased at too rapid a rate to ∞ as the temperature decreases to 0.

In accordance with a remark by NERNST[1]) we are practically forced to assume that for the molecular translatory motion of a gas on approaching to $T=0$ at last the equipartition laws are no more valid. For the determination of the temperature one can then no more rely upon the gasthermometer. A method for the determination of the temperature, which is then suitable in theory, is this that one derives the temperature from the energy density of the radiation which is in equilibrium with it.

We shall consider the equilibrium between the molecular translatory motion of the gas and the radiation subsequently at two temperatures T and $T+dT$. The most obvious assumption is that to an increase of the energy density of the gas an increase of the energy density of the radiation corresponds which is in a finite ratio to the first, in other words that

$$dU=\gamma T^3\,dT, \quad \ldots \ldots \ldots \quad (2)$$

where γ has a finite, and at sufficiently low temperature a constant value. In this equation U may represent the energy of the gramme-molecule of the gas. The molecular volume is supposed not to become ∞ on approaching to $T=0$.

From (2) follows that [2])

$$\text{for } T=0 \quad : \quad \left(\frac{\partial U}{\partial T}\right)_V=0. \quad \ldots \ldots \ldots \quad (3)$$

The equation (2) has the same form as the corresponding relation for a solid. Indeed it could hardly be assumed that the equilibrium between the molecular motion of the gas molecules in colliding against a solid and the radiation would be governed by quite a different law from the equilibrium between the molecular motion in a solid and the radiation.

From (2) and

$$p=\frac{2U}{3V}, \quad \ldots \ldots \ldots \ldots \quad (4)$$

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[1]) W. NERNST, Physik. Z.S. 13 (1912), p. 1066. Cf. also H. KAMERLINGH ONNES and W. H. KEESOM, Math. Enz. V 10, Leiden Comm. Suppl. N⁰. 23, note 51·7.

[2]) It will be noticed that for the validity of (3) a decrease of $\left(\frac{\partial U}{\partial T}\right)_V$ proportionally to T^3, as is indicated by (2), is not required, but that a decrease proportionally to T would be sufficient.

which relation remains valid, follows for $T=0$

$$\left(\frac{\partial p}{\partial T}\right)_V = 0, \text{ hence } \left(\frac{\partial S}{\partial V}\right)_T = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

if S represents the entropy.

If we now calculate the change of entropy which occurs on mixing two ideal gases (i.e. gases, in whose equation of state no members occur which depend on the volume and the mutual attraction of the molecules) by supposing this mixing to take place in a reversible way at constant temperature, it follows from the last mentioned relation that at the absolute zero the entropy change on mixing is equal to 0.

§ 2. The theorem indicated in the former § may be further elucidated by means of relations for the equation of state of an ideal gas which I deduced in Suppl. N°. 30*a* (May '13). It seemed, however, desirable to me as the foundations of the considerations of § 1 not to make more assumptions than are strictly necessary. For against several of the special assumptions of Suppl. N°. 30*a*, particularly against the use of DEBIJE's method in the way as is done there for an ideal gas, more or less serious objections can be made. All the same the deviations from the equipartition laws, which will become apparent in the equation of state of an ideal monatomic gas, are presumably given rightly in a qualitative sense by those relations. Further it seems to me that one may expect with some confidence that the order of magnitude of those deviations will agree with that of the deviations given by the relations mentioned. For this reason it seems to me to be not quite superfluous to indicate here what may be derived for the entropy of an ideal mixture from those relations.

a. From equation (1) of Suppl. N°. 30*a* with (2), (3), and (5) of that paper follows for a *one-component gas*, if molecular rotations and intramolecular motions are left out of account [1]),

$$S = \frac{9N}{\boldsymbol{v}^3_{\max}} \int_0^{\boldsymbol{v}_{\max}} \left\{ \frac{1}{T} \frac{h\boldsymbol{v}}{e^{\frac{h\nu}{kT}} - 1} - \ln\left(1 - e^{-\frac{h\nu}{kT}}\right) \right\} \boldsymbol{v}^2 \, d\boldsymbol{v}. \quad . \quad . \quad . \quad (6)$$

With

$$\xi = \frac{h\boldsymbol{v}}{kT}, \; x = \frac{h\boldsymbol{v}_{\max.}}{kT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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[1]) This expression was already given by H. TETRODE, Physik. Z.S. 14 (1913), p. 212.

and integrating partially as regards the second term under the integral sign, (6) changes into

$$S = 3Nk \left\{ \frac{4}{x^3} \int\limits_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \ln (1 - e^{-x}) \right\} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For large values of x this gives:

$$S = 3Nk \left\{ \frac{4\pi^4}{15} \frac{1}{x^3} - 3x \sum_{n=1}^{n=\infty} e^{-nx} \left(\frac{1}{nx} + \frac{4}{n^2 x^2} + \frac{8}{n^3 x^3} + \frac{8}{n^4 x^4} \right) \right\}, \quad (9)$$

for small values of x:

$$S = -3Nk \left[\ln (1 - e^{-x}) - \frac{4}{3} \left\{ 1 - \frac{3}{8} x + \frac{3}{5} \frac{B_1}{2!} x^2 - \frac{3}{7} \frac{B_2}{4!} x^4 + \dots \right\} \right], \quad (10)$$

if B_1, B_2 .... denote the Bernouillian coefficients.

a. Low temperatures. If of the development (9) we write down the first term only, we may put $x = \frac{\theta_0}{T}$ with θ_0 according to Suppl. No. 30*a* equation (18*a*) or (18*b*). This gives

$$S = aM^3 V^2 T^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

if M denotes the molecular weight, and a a constant which depends on Planck's constants h and k and on the Avogadro number.

According to (11), the volume being kept constant, the entropy approaches to 0 for $T = 0$. It does so proportionally to T^3, which is in agreement with (2). The latter would not have been the case if (see Suppl. No. 30*a* § 4*c*) the zero-point energy had not been introduced in the theory, cf. H. Tetrode, Physik. ZS. 14 (1913), p. 214.

β. High temperatures. Retaining in the development for high temperatures only the first term which gives a deviation from the equipartition laws, we obtain:

$$S = -\frac{3Nk}{2} \ln \frac{8}{3} \frac{\theta_0}{T} + 4Nk + \frac{16Nk}{1575} \frac{\theta_0^2}{T^2}. \quad . \quad . \quad . \quad (13)$$

or

$$S = Nk \left\{ \frac{3}{2} \ln \beta MTV^{2/3} + 4 + \frac{1}{700} (\beta MTV^{2/3})^{-2} \right\} \quad . \quad . \quad (14)$$

where β is a constant depending on h, k, and N.

The additive constant $Nk\left(4 + \frac{3}{2} \ln \beta M\right)$, with which the "chemical constant" is connected, agrees with the expression obtained for it by Tetrode l.c. without the assumption of a zero-point energy.

b. From (11) and (14) the entropy of the molecular quantity of an *ideal mixture*, again leaving molecular rotations and intramolecular motions out of account, may be easily derived if GIBBS' theorem, according to which the entropy of such a mixture is obtained by calculating the entropy for each component as if it were present by itself in the volume occupied by the mixture and adding the values so obtained, is supposed to remain valid when the equipartition laws no longer hold. We then obtain:

α. for *low temperatures*

$$S = aT^3 V^2 \Sigma \frac{M_1^3}{c_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

β. for *high temperatures*, retaining the first term which gives a deviation from the equipartition laws:

$$S = Nk \left\{ \frac{3}{2} \ln \beta T V^{2/3} + \frac{3}{2} \Sigma\, c_1 \ln M_1 - \Sigma\, c_1 \ln c_1 + 4 + \right.$$
$$\left. \frac{1}{700} (\beta T V^{2/3})^{-2} \,.\, \Sigma\, c_1^{7/3} M_1^{-2} \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If at constant volume the temperature continually decreases, at sufficiently low temperatures (for densities of the order of magnitude of the normal density at extremely low temperatures, cf. Suppl. N°. 30*a* § 5*b*) a positive deviation from the equipartition value begins to develop itself. This deviation finally causes the entropy for a mixture also to approach to 0 proportionally to T^3 as shown by (16) instead of becoming $-\infty$.

Physics. — "*Further experiments with liquid helium. H. On the electrical resistance etc. (continued).* VIII. *The sudden disappearance of the ordinary resistance of tin, and the super-conductive state of lead.*" By Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of May 31, 1913).

§ 13 [1]. *First observation of the phenomena. a.* Passing from the investigation of the super-conductive state of mercury to that of the change in the resistance of various other metals when they are cooled to helium temperatures, although I hoped to find more superconductors, I did not think it likely, judging from our experiences

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[1] The §§, tables and figures are numbered successively to those of Comm. VII of this series. (These Proceedings May and June 1913).

with gold and platinum (see Comm. N°. 119, III and Comm. N°. 120, IV of this series) that we should be able to get more than a systematic survey of different cases of additive admixture-resistance (see Comm. VII of this series § 10). Very soon, however, the surprising results with tin and lead were obtained, which we mentioned in Comm. VII § 1 and § 12.

In the first place on Dec. 3rd 1912 we investigated a wire of pure tin, and perceived that this metal too, at helium temperatures became super-conducting.

The tin was of the specially pure kind supplied by KAHLBAUM. It was melted in a vacuum and poured into a glass capillary U-tube. The capillary tube had tin branches at either end, by which the conducting wires and the measuring wires were attached. The resistance at the ordinary temperature, 290° K., was 0.27 Ω.

We found that at the boiling point of helium a small ordinary resistance $1.3 \cdot 10^{-4}$ Ω remained. At 3° K. this had disappeared ($< 10^{-6}$ Ω) and when the field of temperature between 4°.25 and 3° K. was gradually gone through, we found that the disappearance took place suddenly at 3°.78 K.

In order to be better able to judge of the micro-residual resistance, we tried to make a tin wire of greater resistance, in the same way in which we had formerly succeeded in making a long thin lead wire [1]). A steel core was covered with a substantial layer of pure tin, and turned down on the lathe. Then with a razorshaped chisel a thin spiral shaving was cut off [2]). This method, which seemed preferable to drawing (comp. § 14*a*) by which the metal might undergo a greater change, yields without difficulty wires of 0,01 mm². section. Several of these wires were then joined into one long wire by melting them on to eachother, during which it was necessary to carefully avoid the possibility of oxide being introduced into the surfaces to be united. The tin wires, one of which 1.75 m. long had a resistance of 19.2 Ω, and the other 1.5 m. long a resistance of 6,7 Ω, were wound upon glass cylinders, between a spiral of silk thread which separated the windings of the tin thread from each other. Leading wires of tin fastened to the up turned ends of the wire, were led downwards through the liquid and attached to copper wires. With these resistances immersed in liquid helium the

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[1]) KAMERLINGH ONNES and BENGT BECKMAN. Comm N°. 132*c*. Dec. 1912.

[2]) A few of the tin wires first made did not become super-conducting; the inferior method of working the metal had perhaps caused additive admixture resistance, or more probably very insufficient continuity of material.

sudden disapparance was observed when the temperature fell to $3^\circ.806$ K. (boiling under 47 cm. mercury pressure). At $3^\circ.82$ K. the resistance of one was still 0.0183 Ω, of the other 0.00584, at $3^\circ.785$ K. of both $< 10^{-6}$ Ω. In this case too the highest limit for a possible micro-residual resistance was thus very low. We may put

$$\frac{w_{3^\circ.8\,K.}}{w_{273^\circ K.}} < 10^{-7}.$$

Besides the sudden disappearance of the resistance of the wire, we also observed, as in the mercury thread, that for each temperature below the vanishing point a threshold value for the current density[1]) determined by this temperature, (in the case of the last mentioned wire the threshold current was 0.28 amp. at $3^\circ.785$ K.) could be fixed, below which the current passes without any perceptible fall of potential, and above which it is accompanied by potential phenomena, which (see § 14) increase rapidly with the increase of the excess of the current above the threshold value. In a word, the tin wire behaves below the vanishing temperature of the tin, $3^\circ.8$ K., qualitatively precisely the same as a thread of mercury below the vanishing point of that metal.

β. Lead of Kahlbaum, made into a wire in the same way as the tin, 1.5 m. long and 10.8 Ω resistance at ordinary temperature, when it was immersed in liquid helium appeared to be super-conducting, without the necessity of reducing the pressure at which the helium boiled. When the temperature was raised as far as the cryostat permitted, that is to $4^\circ.29$ K. (the pressure was raised 11 cm. mercury above 76 cm.) the lead remained super-conducting. The temperature at which the ordinary resistance of the lead disappears will probably, as indicated in § 15, not be far above the boiling point of helium.

Whether this disappearance, as with mercury and tin, also takes place suddenly, has yet to be investigated. For temperatures below 14° K., where lead has still a relatively high ordinary resistance, and above $4^\circ.3$ K. where it has disappeared, we do not yet possess a satisfactory cryostat. At the temperature just mentioned of $4^\circ.29$ K. we found that the threshold value of the current was not yet reached at 1.3 amp.

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[1]) Concerning the dependence of the threshold value upon the dimensions of the wire and the conditions under which the heat is given off, further investigation is needed.

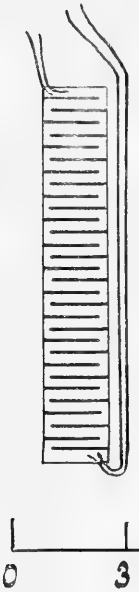

Fig. 8

Fig. 9

γ. Besides lead and tin, amalgamated tin foil was investigated. We examined a layer of it spread out on a mirror glass, in which layer grooves were made in the manner shown in fig. 8. In helium boiling at atmospheric pressure, it appeared to have lost the ordinary resistance (2.3 Ω at 290° K.). At 4°.29 K. we found 0.12 amp. for the threshold value of the current, and a potential of $1.3 . 10^{-6}$ volt, at 0.30 amp. $19.8 . 10^{-6}$ volt, and at 0.363 amp. $34.6 . 10^{-6}$ volt.

It is worth noticing that this amalgamated tinfoil becomes more easily superconducting than either tin or mercury. Perhaps the soft tin-amalgam, though a solid solution (of mercury in tin), has this property. This would only need to become a continuous whole in order to provide a nonresisting path for the current beside that of the free mercury (comp. (§ 9) or tin that might be present in the tin foil.

§ 14. *Further investigation of tin.* The further investigation of tin and lead does not form by any means a complete whole yet. Several of the measurements we had in view were failures, so that the results attained are very disconnected; nevertheless, in connection with our experiments with mercury, I think them worth communicating.

a. Methods of working the tin. In the previous § we said that working the tin into a spiral shaving did not interfere with the sudden disappearance of the resistance. What is of even more importance is that the rolling out of the wire to a thickness of 0.01 mm. has not any influence upon the super-conducting state either, so that we may feel confident that a very thin nonresisting tinfoil could be made[1]).

We must remark that in working tin, heating must be avoided. The increase of hardness which is caused in the drawing of metals by the compression and stretching, which is accompanied by an

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[1]) The resistance of commercial tin foil, pasted on glass and cut out as in fig. 9, appeared not to become zero.

increase of resistance and decrease of the temperature coefficient, is removed in gold and platinum for instance, by heating. With tin, on the other hand, heating is injurious, it causes the resistance to increase [1]), moreover, it causes thin wires to go into angular forms [2]). The threads we used were, therefore, not heated after being worked, and showed regular curvatures when bent.

β *Potential phenomena in the super-conducting state.* The following observations allow us to judge of the highest limit of the possible micro-residual resistance, and of the potential differences above the threshold value of the current density just below the vanishing point. They were made with a branching tin wire exactly like the one used in the experiments with mercury of Table IV and V in Comm. VI of this series, § 6 and 7. The resistance consisted of a principal wire W_C 4 m. long, and mainly 0.0097 mm². section [3]) with two

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[1]) According to Tammann and his school, the crystals are shattered by wire drawing, and arranged in such a way that in the cases meant the resistance increases. By heating, larger crystals are again formed, and the resistance resumes its original value. In the investigations of Kamerlingh Onnes and Clay, (Comm. N⁰. 99*b* § 4, June 1907), it is pointed out that the additive resistance of platinum and gold wires is always found greater by continued drawing even after heating to glowing. We attributed this to the acquiring of admixtures through the drawing. In gold it is possible to test for such small quantities of admixture as are here of importance. In gold wires carefully drawn by Heraeus (Comm. N⁰. 99*c* § 2, June 1907), under repeated treatment with acids, larger quantities of admixtures were found in proportion as the resistance fell less at reduction to hydrogen temperatures. At the same time it is possible that the drawing itself has an influence. Henning (Ann. d. Phys. 1913), thinking as we do, attributes the difference found with his platinum thermometers in the temperature coefficient from that found by us, to a larger amount of admixtures in our thermometer. The difference becomes greater still, when we consider that Henning's wire (0.05 mm.) was drawn out further than ours (0.1 mm.) (which is of importance in the application to thermometry). As mentioned above and as we found confirmed in comparing the wires Pt_I (0,1 mm.) and Pt_d (0,05 mm.), thinner wires fall less in resistance, a result by which we also explained, l. c., why Holeorn's thick wires (0.2 mm.) showed a greater fall than ours. Our wires were at the time most carefully drawn by Heraeus from the purest platinum supplied by him. The platinum obtained by Heraeus later on may have been even purer. Improvement may also have been made in the method of drawing the wires.

[2]) Where broken, tin wires exhibit comparatively large crystals. See also § 15 note 1.

[3]) In this investigation the section is deduced from the length of the wire and the resistance at ordinary temperature. We only ascertained, whether this agreed approximately with the result of direct measurement. The values given are thereore only to be considered as rough mean values.

sentinel wires W_{SA} and W_{SB}[1]) of 0.8 m. length and about 0.02 mm². section, wound round a glass tube and insulated with silk. We found, (Febr. 1913)[2]):

TABLE VIII.

Resistance of a bare tin wire at, and a little below 3°.8 K.
Section of w_C: 0.0097 mm².

T	w_{SA}	w_{SB}	w_C
	Current density 0.61 amp./mm² in C.		
3°.85 K.	$6.84 \cdot 10^{-3}\,\Omega$	$6.50 \cdot 10^{-3}\,\Omega$	$69.6 \cdot 10^{-3}\,\Omega$
.82	5.50	0.90	34.9
.79	2.82	0.03	1.23
.785	1.5	0	0
.78	0.7	0	0
.75	0.15	0	0
.74	0.02	0	0
.72	0	0	0
	Current density in C 154 amp./mm² (and higher?)		
1°.6	0	0	0

With a coil of 252 windings of tin wire insulated by picëin (see § 16) of 0.014 mm². section, (with pieces of 0.02, 0.012 and 0.03) and 79 Ω resistance at ordinary temperature 290° K., the disappearance of the resistance was followed, at three different current strengths as in § 8 was done with mercury. We found:

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[1]) The object of the sentinel wires was the same as in VII § 6. We had namely calculated on sending much stronger currents through than we actually did, and on that supposition it was necessary to make sure that no JOULE heat penetrated to the wire from elsewhere.

[2]) In one of the sentinel wires W_{SA} there is obviously a thinner place which causes locally a much greater current density than the mean. Probably the same case occurs here as in the experiments with mercury in Table IV, but here the disappearance of the resistance at lower temperature makes it improbable that the tin wire should be interrupted by a foreign resistance.

TABLE IX.

Disappearance of the resistance of a tin wire, under reduced giving off of heat, at different currents.

T	0.004 amp.	0.04 amp.	0.4 amp.	0.6 amp.	1.0 amp.
3°.82 K.	0.0533 Ω	0.0535 Ω	0.0536 Ω		
.805	500	534	536		
.79	488	533			
.785	425				
.78	162	508			
.765	0.00137				
.75	0.00005	0.0039			
.74	1	14	0.0532		
.72	0.000000	0.00025			
.70					
.68		0.000012			
.66		0.000000	0.0050		
.64					
.54			38		
.42			22		
.28			10		
$.12^5$			0.0002		
2.69			0.000012		
.35			0.000000		
1.6				0.000000	great

This table gives in general the same as fig. 6 and 7 of § 8. The disappearance of the resistance extends over a much larger field of temperature than with the mercury thread, probably because the giving off of heat is considerably reduced by the winding up of the wire protected by picëin; which is probably also the reason why at the lowest temperature the strength of the current cannot be raised above 0.8 amp. and the threshold value of the current density therefore only reaches 56 amp/mm^2.

γ. Experiments concerning the influence of the contact with an ordinary conductor of a metal which can become super-conducting, upon its super-conducting properties, were in continuation of those of § 10 made with tin in two different ways, first with a german silver tube, which was tinned, and through the layer of tin of which a spiral was cut, and second with a constantin wire which was tinned. In the first experiment the resistance did not disappear, in the second, as already said in § 10, it did; from which we conclude that the continuity of the layer of tin in the first case was not sufficient. In the second experiment the threshold value was, however, also very low, even at the lowest temperature 1.°6 K. it remained below 0.095 amp. for the bare wire immersed in liquid helium. It is simplest to assume in the mean time, that the layer of tin becomes super-conducting, but that the section of it, which was, deduced from the resistance, 0,0125 mm²., according to measurements down to 0,1 mm²., was very small here and there. There was in this case no reason to suppose a want of contact between tin and constantin, as in the corresponding experiment with mercury between it and the steel.

§ 15. *Further examination of lead.* In the first place we will mention a few experiments on the heating of a wire which was at a temperature below the vanishing point, which correspond to those

TABLE X.
Potential differences in a lead wire carrying a current
$l = 6$ M., section $= 0.014$ mm².

T	Current density in amp/mm²	Potential difference in microvolts
1°.7 K.	560	0.0
	645	0.2
	675	3.5
	695	5
	710	6
	720	10
	750	19
	791	± 40
	> 790	very great

in Table VI for mercury. The lead resistances were arranged exactly like the tin resistances described in § 14, the bare wires were wound upon glass between silk. With a wire of 0.025 mm². section (10.8 Ω resistance at ordinary temperature) containing six joints, which were made with a miniature hydrogen flame, we ascertained that joints do not interfere with the experiments. The results (Febr. 1913) with one of the wires (92 Ω at ordinary temperature) are contained in Table X (the observations were confirmed later on repetition).

A similar experiment with the wire containing six joints at less low temperature gave;

TABLE XI.

Threshold value of current density for bare lead wire of section 0.025 mm².

T	Threshold value in amp/mm²
4°.25 K.	> 420
	< 940

At a current density of 940 the wire was dammaged (calefaction?) and upon repetition it appeared that it was broken.

Similar conditions of external conduction of heat to those of the tin coil described in § 14, prevailed in a lead wire (see § 16) of

TABLE XII.

Potential difference in a lead wire carrying a current with reduced external conduction of heat.
$l = 55{,}5$ M. section = 0.014 mm²

T	Current density in amp/mm²	Potential difference in microvolts
4°.25 K.	33	0.03
	36	0.65
	38	1.75
	40.2	7.35
	41.3	22.0
1°.7	60	3.7

1000 windings (resistance at ordinary temperature, 290° K., 773 Ω) insulated by silk soaked in liquid helium. We found: (See table XII p. 681).

Judging by this we may perhaps estimate that the lower limit of

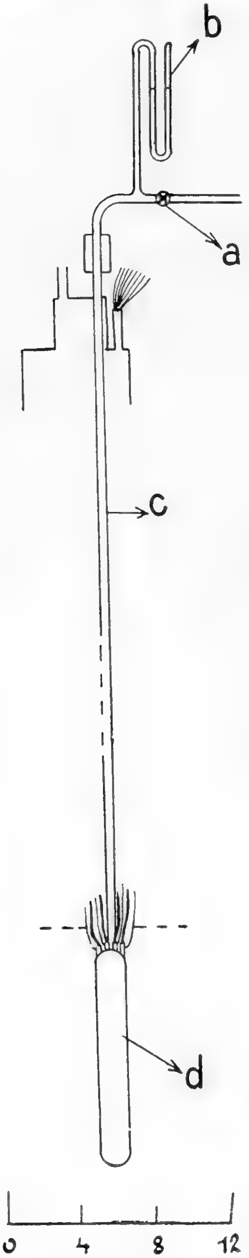

Fig. 10.

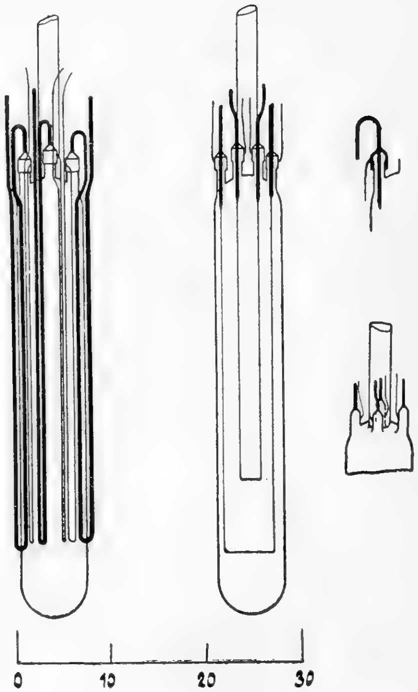

Fig. 11.

the threshold value at 4°.25 K. given above cannot be raised much, and that the vanishing point for lead lies at about 6° K.

Further, measurements were made with lead wires placed in a vacuum, the object of which is obvious by § 12. The apparatus which served for this consists (see fig. 10 and fig. 11, face view and diagram of *d* with detail figures) of a glass reservoir immersed in liquid helium, carried by a long narrow glass tube fixed into the lid of the cryostat. The reservoir *d* can be evacuated through the tube *c* (the tap *a* allows it then to be connected to a tube filled with charcoal which is immersed in liquid air); through the indicator gauge *b* we can make sure that the apparatus is not cracked in cooling.

In the apparatus shown in the fig. there are two lead wires (see diagram); we were only able to do the measurements with one. Four short tubes are blown into the upper part of the reservoir to receive the lead wires (see detail figures); upon these tubes after platinizing and copperplating caps are soldered with tin into which the thicker top ends of the wires are soldered with Wood-metal[1]).

Rolled out lead wires are fastened to the wires that project from the covers, and run down along the reservoir, insulated from each other with silk and then up again through the liquid helium.

We found with a part of the wire of Table XI:

TABLE XIII.

Threshold value of current density of a lead wire in vacuo; section $^1/_{70}$ mm^2.

T	Current density in amp/mm^2
4°.25 K.	> 270

The experiment is incomplete as the threshold value was not reached.

We made similar apparatus with tin wire; the observations with tin in vacuo have, however, not succeeded yet.

§ 16. *Remarks in connection with the experiments with tin and lead.*

a. Our results with tin and lead make it seem probable that

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[1]) It is not possible to solder tin wires into the covers with Wood-metal: as coming in contact with the tin the melted Wood-metal, as it seems, penetrates by capillary action amongst the tin crystals which makes the wire brittle and break in two. The tin wires must therefore be melted to the tinned covers, which is possible, by their being provided like the lead wires with sealed on thicker ends.

all metals, or at least a class of them, if they can be procured sufficiently pure, pass into the super-conducting state when reduced to a low enough temperature. Perhaps in all it would also be suddenly. But the additive admixture-resistance which can be caused by mere traces of admixtures, will in general make the detection of the phenomena a difficult one.

β. A number of experiments with resistance-free conductors of which several suggest themselves at once, now that we can use the easily workable super-conductors tin and lead, can be undertaken with good prospect of success[1]).

In this way the preparing of nonresisting coils of wire, with a great number of windings in a small space, changes from a theoretical possibility into a practical one. We come to new difficulties when we want not only to make a nonresisting coil, but to supply it as a magnetic coil with a strong current[2]).

I have been engaged for some time making a preliminary estimation of these difficulties[3]).

The coils mentioned in § 14 and § 15 were made chiefly for this purpose. The first of tin wire insulated with piceïn, contained on 1 cm. length in a layer of 7 mm. thickness 300 windings of $^1/_{70}$ mm^2. section (the resistance at ordinary temp. was 79 Ω). While a current of 8 amp. could be sent through the wire before it was wound when immersed in liquid helium, without reaching the threshold value of current density (see § 14) the coil came to the threshold value at 1.0 amp. The number of ampere windings per cm^2. of a section through the axis was about 400. The second coil was wound of lead wire of $^1/_{70}$ mm^2. section, and contained in a length of 1 cm. 1000 windings in a layer of 1 cm. thickness. The resistance at ordinary temperature was 773 Ω. The insulation of the wires in each layer was obtained by silk threads, between the different layers a thin piece of silk was placed. I thought that the liquid helium penetrating into the coil through this texture would cause the heat to be given off more easily all over the coil, while

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[1]) In our first paper about the disappearance of the resistance of mercury we mentioned that this opened a new field of experiment. That mercury is liquid at ordinary temperature was, however, a serious hindrance to entering it.

[2]) A coil of this kind one would wish to place in the interferrum of a very large electromagnet of Weiss, in the same way as the auxiliary coils contemplated by him, in order to further raise the field. The field that is added by the coil would in that case have to be greater than what would be sacrified by enlarging the interferrum to make room for the cooling appliances.

[3]) A possible difficulty was pointed out in note 2 § 4.

it was not certain (comp. the remarks about mercury in glass in § 7 and § 11 Comm. VII of this series) that the picëin remained adherent to the tin wire everywhere. Through this coil a current of 0.8 amp. (see § 15) could be sent, without the threshold value being reached. The number of ampere windings per cm^2. was then about 800. If the disturbing potential phenomena had not been greater than with the shorter wire of the same section which was washed by liquid helium over its entire surface, and if the difficulty mentioned in note 2 § 4 does not come into play, it would have been possible to supply this coil with up to 9000 ampere windings per cm^2. If, therefore, the potential phenomena which frustrated this in the experiment reported, in accordance with the opinion expressed in Comm. N°. VII of this series, particularly in § 11, may be ascribed to "bad places" in the wire, and if we may therefore be confident that they can be removed (for instance by fractionising the wire) and if moreover the magnetic field of the coil itself does not produce any disturbance (note 2 § 4) then this miniature coil may be the prototype of magnetic coils without iron, by which in future much stronger magnetic fields may be realised than are at present reached in the interferrum of the strongest electromagnets [1]).

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[1]) J. PERRIN (Soc. d. phys. 19 Avril 1907) made the suggestion of a field of 100000 gauss being produced over a fairly large space, by coils without iron, cooled in liquid air. Ch. FABRY (Journ. d. Phys Févr. 1910) worked out this idea. He finds that the energy absorbed in such a coil, in watts is represented by the formula

$$W = \varrho \eta a H^2 K^{-2}$$

where a is a length in centrimetres, which determines the size of the coil, for a cylindrical one the radius of the internal space, η the ratio of the metallic area in a section through the coil at right angles to the windings to the area of this section, K a purely numerical coefficient, which depends upon the form of the coil, and which in cylindrical coils with wire of equal section does not differ much from 0,18, ϱ the specific resistance of the metal of the windings in ohms. centimetre, H the magnetic field in gauss.

In order to get the desired field of 100000 gauss in a coil with an internal space of 1 cm. radius, with copper as metal, and cooling by liquid air 100 kilowatt would be necessary, putting K at 0.20 and η at 1,5 (which last number might well be 6 times as large). The electric energy supply, as FABRY remarks, would give no real difficulty, but it would arise from the development of JOULE heat in the small volume of the coil to the amount of 25 kilogramme calories per sec. which in order to be carried off by evaporation of liquid air would require about 0,4 litre per second, let us say about 1500 litres per hour.

We may add to FABRY's objection that the preparation of 1 litre of liquid air per hour is at present to be reckoned as requiring not much less than $^1/_2$ K. W. According to this standard, 7 times as much work would be necessary for the

γ. Certainty that the potential phenomena observed are due to such imperfections in the wire would be of no less value for another tempting group of experiments. As soon as the super-conductivity of mercury was established, the question forced itself upon me, in connection with the great value which according to the electron theory of metals is ascribed to the free path of the electrons[1]) (comp. § 12 β), whether electrons moving at speeds by which they cannot penetrate a thin plate, e.g. a LENARD's window of solid mercury, at temperatures near the ordinary temperature[2]), or at least not without a change of direction, would be able to do this better if the foil were

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cooling than for the current. By a judicious use of the cold of the vapours this number can be reduced, but the proportion will remain unfavourable.

Moreover, as FABRY shows, the dimensions determined by a, to make it possible for the heat to be carried off, would need to be much larger, by which at the same time the amount of liquid gas used becomes greater. The cost of carrying out PERRIN's plan even with liquid air might be about comparable to that of building a cruiser!

If we calculate in the same way the cooling with liquid hydrogen in the case of silver and if we assume that the resistance of silver (according to KAMERLINGH ONNES and CLAY) at the boiling point of hydrogen is 0,009 of that at the ordinary temperature, we arrive at a more favourable figure, namely, that at $a = 1$ cm., 700 liters of liquid hydrogen would be needed per hour, but the ratio of cooling work and electric work becomes more unfavourable yet, putting the preparation of a litre of liquid hydrogen in the same way as above at $1^1/_2$ K. W. But the figure for liquid hydrogen would also on the ground mentioned above have to be considerably increased. Although an installation which will give as much liquid hydrogen as is necessary for the cooling could be made after the pattern of the present Leiden plant, it would be of such an extraordinary size that with liquid hydrogen also, the method described perhaps involves more difficulties than a further increase of the size of the coil, in order to be able to cool with running water (as introduced by WEISS) while this method also has its advantages with a view to the use of the field.

The possibility of using the super-conductors tin and lead, gives a new departure to the idea of PERRIN of procuring a stronger magnetic field by the use of coils without iron. With super-conductors no JOULE heat needs to be carried off (or at any rate only 10^9 times less than with ordinary conductors) and thus with currents below the threshold value the difficulties mentioned above disappear. If the conditions mentioned in the text can be fulfilled, then even a coil of 25 cm. diameter of lead wire, constructed as the one in § 15, immersed in helium, could give a field of 100000 gauss, without perceptible heat being developed in the coil. Some such apparatus could be made at Leiden if a relatively modest financial support were obtained. In the mean time this remark may serve to put the problem of very strong magnetic fields which are becoming indispensable for various investigations in new form.

[1]) Comp. note 3 p. 1113. Leiden. Comm. N^0. 119. Febr. 1911.

[2]) Whether the same electron passes through, or whether the movement is carried from the one to the other, does not affect the experimental question.

superconductive. Now that super-conducting plates of tin and lead can be made, the experiments on this subject are made practicable, and the plan of making these has assumed a promising form, since I have obtained the prospect of doing it with **Lenard** himself, which I highly value. If the potential phenomena are caused by local disturbances, we may expect that in experiments with thin plates, by a correct choice of the places to be experimented upon, they will be of little importance. If, as might be imagined according to § 4, the potential phenomena are connected with peculiarities in the movements of the electrons, then they would be of prime importance in phenomena such as we have here under consideration.

d. The correspondence of the potential phenomena in tin and lead to those in mercury is very striking. As regards tin, it was stated already in § 13*a*, and further investigation has confirmed it and also extended to lead. All the considerations with regard to them for the case of mercury can thus immediately be applied to tin and lead. On the other hand the latter may serve to elucidate the doubtful points in mercury.

With the bare tin wires at 4°.25 K. measurements were made which acquaint us with the amount of heat, given off to the liquid helium above the vanishing point; whether it is proportional to the surface of the wire, as is to be expected, when the heat is mainly given off to the liquid, could not be settled yet. With the rolled out tin wire, with which the various measurements were successful, it was great, which corresponds to the fact that here the ratio between the heat-conveying surface and the heat developed is very favourable. It was estimated at 0.5 watt per 1 degree difference of temperature. Still at 1°.6 K., 1.4 microwatt caused a local rise of temperature to the vanishing point. As in § 11 we deduce from this that the whole development of heat is local. The hypothesis that in this way "bad places" show themselves is confirmed by the fact that through a wire like this at the boiling point of helium, therefore above the vanishing point, a current of 9 amp. could be sent, and all the **Joule** heat was absorbed by the liquid helium, while with a current only a little stronger the wire gave way (presumably by the forming round the wire of a vapour bubble in the helium, which caused calefaction in the wire).

The different threshold values for the bare lead wire and the lead coil § 15, and for the bare tin wire and the tin coil § 14, may throw light upon the influence of more or less easy conditions of heat loss. The phenomena at the disappearance of the resistance with the bare tin wire with sentinel wires make the hypothesis followed out in § 12 improbable, namely that the mercury below the vanishing point comes away from the glass or at least does not give off heat to it at a difference of temperature. The correspondence of the disappearance of the resistance in the tin wire with sentinel wires and in the mercury thread is explained most simply by assuming a local rise of temperature in both, while for both below the vanishing point the same opportunity remains for giving off heat, but does not take place owing to absence of rise of temperature.

Here, therefore, the "bad places" mentioned in § 11 (comp. § 12*a*, note 1 p. 118) would again remain as the sole explanation. It is however suspicious that in the coil of lead wire at 1°.6 K. 56 amp./mm^2. was found as the threshold value, while with lead in a vacuum 270 amp./mm^2. at 4°.26 K. was reached without a trace of potential phenomena.

Finally we point out that the threshold values of current density far below the vanishing point in the wires of the three different metals differ very little. We found for the highest limit of the possible micro-residual resistance determined by the threshold value in proportion to that at the ordinary temperature

$$\text{with mercury} \quad \frac{w_{2^{\circ}.45\,K}}{w_{273^{\circ}\,K}} < 2.10^{-10}$$

$$\text{tin} \quad \frac{w_{1^{\circ}.8K}}{w_{273^{\circ}\,K}} < 6.10^{-10}$$

$$\text{lead} \quad \frac{w_{1^{\circ}.8K}}{w_{273^{\circ}\,K}} < 0.5\ 10^{-10}$$

In view of so much correspondence and such regularity of the character of all the potential phenomena, it still remains doubtful whether besides the disturbances which we have adduced to explain them, there may not be at the bottom of them peculiarities in the movement of the electrons, which may be more clearly revealed by the experiments indicated in γ.

Having completed the series H of my experiments with liquid helium I wish to express my thanks to Mr. G. Holst, assistant at the Physical Laboratory, for the devotion with which he has helped me, and to Mr. G. J. Flim, chief of the technical department of the cryogenic laboratory, and Mr. O. Kesselring, glassblower to the laboratory, for their important help in the arrangement of the experiments and manufacturing of the apparatus.

Physics. — "*Magnetic researches. X. Apparatus for the general cryomagnetic investigation of substances of small susceptibility.*" By Prof. H. KAMERLINGH ONNES and Dr. ALBERT PERRIER. Communication N°. 139*a* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of October 25, 1913).

§ 1. *Introduction.* This paper contains the full description of the apparatus used in the investigation of Communication III (Comm. N°. 122*a*, continued in IV, Comm. N°. 124*a*) of this series (Proceedings of May 1911). Various circumstances have retarded the extensive description which was promised there instead of the rough sketch.

The construction of the apparatus to be described forms part of a more general scheme to gradually obtain the necessary appliances for the investigation of weak magnetisation at low temperature. In doing this we did not confine our attention to special measurements, but intended to enlarge with as many appliances as possible the almost completely unknown "technique" of investigations in this field.

On the one hand the measurement of magnetic forces, on the other that of magnetic couples suggest themselves. The ballistic method (measurement of flux) is only applied in the study of ferromagnetism [1]).

The method of couples is specially suitable for crystals and for isotropic bodies, which by their shape are seemingly magnetically anisotropic (e. g. ellipsoids). The apparatus with which our first measurements on the susceptibility of liquid and solid oxygen were made (Comm. N°. 116, Proceedings April 1910) is based on this method.[2]) In a modified form this piece of apparatus will, we hope, be soon utilized in the cryomagnetic investigation of crystals.

In measuring forces a non-homogeneous field is used. Two cases have to be distinguished here.

For an object of small dimensions (the volume of which is v and the volume-susceptibility K) placed in the plane of symmetry between the poles of a magnet the force in the direction of the middle of the interferrum is given by

$$F = vKH \frac{\partial H}{\partial y}$$

where H indicates the intensity of the field and y the coordinate at right angles to the field.

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[1]) In some cases which we will not dwell upon here this method might be resorted to.

[2]) The apparatus used by WEISS and KAMERLINGH ONNES for the investigation of ferromagnetism at low temperature (Comm. N°. 114) belongs to the same type.

For an object in the shape of a rod of uniform section s, the axis of which is in the plane of symmetry of the poles and passes through the middle of the interferrum, the relation is

$$F = \frac{K}{2} s \left(H''^2 - H'^2 \right)$$

if H'' and H' are the values of the field-strength at the ends of the rod. When dealing with bodies of small dimensions by the method of FARADAY, the spherical object is placed where $H \frac{\partial H}{\partial y}$, therefore the force is a maximum. This is the method of procedure specially used by CURIE in his classical researches.

The rod-method, though applied long ago for measuring the susceptibility of liquids by QUINCKE's method, was hardly used at all in investigations on solids until 1910, when PASCAL adopted it in his important series of magneto-chemical researches [1]).

This is certainly curious, as the principle of the method is very simple and direct, but even more so as the disposition itself offers important advantages over the other methods. If one end of the rod is placed in the middle of the interferrum and care is taken that the other end is as far removed from it as possible, H'' obtains a maximum value and H' remains a quantity which may be neglected or need only be taken into account as a correction.

The susceptibility is thus given by a single field-strength which is much more easily determined than the product $H \frac{\partial H}{dy}$, which has to be derived from several values of H, not to mention the fact, that the measurement itself of H in the middle of the interferrum, where the field is most nearly uniform, can be carried out much more accurately than at the point where the field is least uniform. An *absolute* measurement by this method can therefore lead to a much more trustworthy result. Moreover in using a rod a much higher *sensibility* can be obtained, on the one hand because a larger quantity of the substance can be utilized, on the other hand because the intensity of the field in the middle of the interferrum can be raised to a much higher value without any objection, which is not by any means the case in the other method. Finally, as the field near the middle of the interferrum can usually be made approximately homogeneous over a space of 1 cc., it is of no great importance at what point exactly within that space the end of the rod

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[1]) P. PASCAL, C. R. 150, p. 1054. 1910. The priority of this application belongs to GOUY. C.R. 109, p. 935. 1889.

under investigation is placed, so that as regards this a rough adjustment will be sufficient; the exact opposite holds when it is desired to place a body at the place of maximum action.

There are cases, however, in which only the method of maximum attraction can be applied, e.g. when the susceptibility depends on the field or when the available quantity of the substance is limited (e.g. on account of its rarity).

On the ground of the above considerations we have made it our object to construct a piece of apparatus *which in the first place is suitable for measurements with objects in the shape of an elongated cylinder, which may further, without important change, be adapted to the study of small objects placed at the point of maximum-attraction and finally, in addition to being suitable for solids, may also be used for the investigation of liquids, either by enclosing them in the movable part of the apparatus or by surrounding it as a bath.*

The ease with which our apparatus may be adapted to the various requirements has shown itself a great advantage in our experiments [1]).

§ 2. *General arrangement of the apparatus* (comp. figure and perspective drawing). The main part of the apparatus is a *carrier* movably suspended along the axis of an enclosure which has the shape of a body of revolution. This enclosure is closed airtight, seeing that it must be capable of being exhausted and that it must be possible to maintain throughout the apparatus any pressure below atmospheric. This requirement from the side of cryogenics has its influence on the choice of most other parts.

The carrier the motion of which is guided along the vertical, carries at its lower end the experimental object which is placed between the poles of an electro-magnet with horizontal axis. The magnetic attraction or repulsion acts along the vertical and is *measured* by compensating it by means of the electromagnetic attraction of two co-axial magnetic coils, one of which is attached to the carrier while the other one is fixed. The force between the two coils is given by

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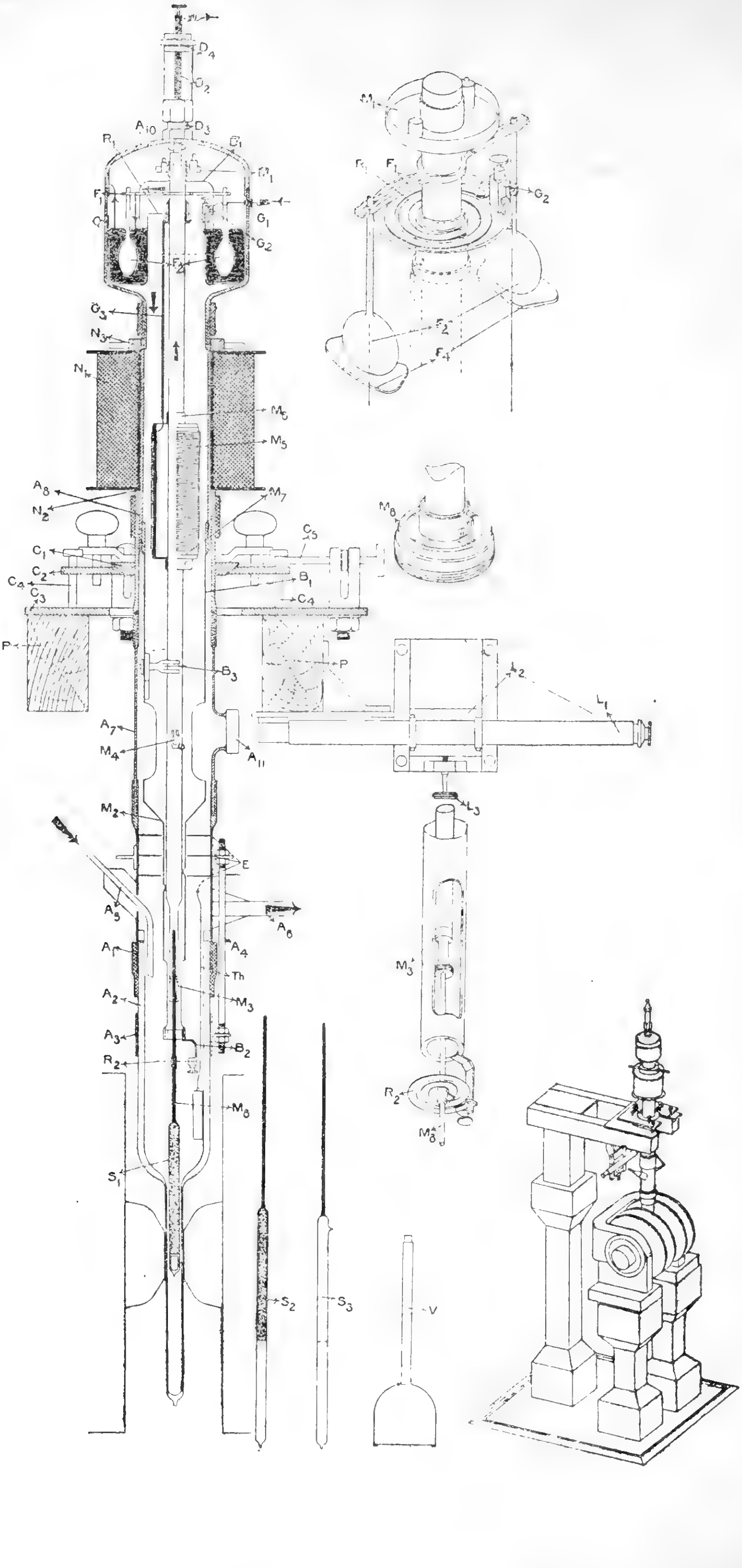
[1]) We may here recapitulate the various apparatus which in the mean time form the complete scheme planned by us:

depending on the use of couples	*a.* apparatus with ellipsoid (Comm. N^0. 116) *b.* ,, for crystals (to be constructed)
depending on the use of forces	*c.* hydrostatic apparatus (Comm. N^0. 116) *d.* apparatus for objects in the shape of spheres or cylinders (this Comm.)

a. has been used for liquid and solid oxygen, *c.* for liquid gases, *d.* for liquified or solidified gases and various solids.


D₄
D₂
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M₃
R₂
M₈

$F = c i_m i_f$, where i_m and i_f represent the currents in the movable and fixed coils and c is a constant which is determined once for all by using known forces (weights) [1].

The electromagnetic compensation has for its sole object making a balance with the forces to be measured: the weight of the carrier itself is balanced *hydrostatically* by means of two floats immersed in mercury; the principle is therefore similar to that of a constant-volume hydrometer.

§ 3. *The various parts of the apparatus.*

a. The enclosure of the cryostat. The space inside the enclosure A of the apparatus is divided by screens E, which prevent exchange of heat between the two parts. The cryogenic part below the screens contains everything connected with the establishment of low temperatures, in the chamber above the screens which remains practically at constant temperature, all the delicate parts for the measurement of the forces are brought together.

The wall of the cryogenic space below E is of german silver. It is joined airtight by means of the india-rubber ring A_1 to the vacuum glass A_2 which contains the bath of liquid gas. The liquid gas is supplied by the german silver tube A_5, the vapours are carried off by A_6. The steel capillary of a heliumthermometer Th is soldered through the wall of the cap.

The upper part of the vacuum-glass is comparatively wide (6 cms), so that the liquid level falls very slowly during the evaporation, which as we shall see is of importance. By means of the copper ring A_3 and the rods A_4 the vacuumglass is firmly connected to the cap, that the considerable forces arising from changes of internal pressure may not change its position.

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[1] For keeping in equilibrium an apparatus of the general type under consideration any kind of force may be used which can be changed gradually without touching the carrier. We can thus work equally well with a given compensating force (definite weights) and changing field (regulating the current through the electromagnet) as with a given field and changing electromagnetic compensating force. When our apparatus was first constructed we did not possess the necessary appliances for accurate field-measurements, and in examining the dependence of the phenomena on the temperature we had to make ourselves independent of the change of the field by confining ourselves to the investigation of the magnetisation at different temperatures at a few field-stengths chosen beforehand and kept constant each time during the experiments

For a modification in which the electromagnetic compensation is replaced by a compensation by weights we refer to a forthcoming description of the apparatus which was used in their investigations by Kamerlingh Onnes and Oosterhuis (Comm. n⁰. 129*b* etc.).

The part of the enclosure above the screens E is entirely of brass with the exception of tube A_7, which is glass.

At A_8 and at the joint with the upper part of the enclosure above N_3, A_9, (the letter is omitted in the figure,) the parts fit each other with friction, which is of great convenience in the building up of the apparatus.

At the upper end the enclosure A is enlarged to a wide chamber containing the parts which serve to keep the carrier afloat. It is closed by an arched cover A_{10}, which again fits on the wall with friction. To this part of the enclosure is attached the german silver tube $B_1 B_2$ which narrows down towards the bottom and to which is fastened at B_2 the spring which guides the movable carrier in a vertical direction and the two stopping pins B_3, which prevent the carrier from moving too far up or down. [1])

The enclosure further serves to suspend the entire apparatus from two horizontal beams; by means of the ball socket $C_1 C_2$ the direction of the axis of the apparatus may be changed, without altering its height. The plate C_2 bears with three adjusting screws C_4 on the ground plate C_3, which in its turn is fixed to the beams, and may be shifted in a horizontal plane in two directions at right angles to each other by means of the screws C_5. With the adjusting screws the apparatus may be moved 3 cms up or down; this is necessary in using FARADAY's method in order to *find* the maximum force by displacing the apparatus with respect to the electromagnet.

b. The movable carrier with adjuncts. In the figure the carrier is indicated by M. It consists of a long thinwalled tube of brass, at the same time light and firm, lengthened by a narrow german silver tube which at its end carries a thread M_3. The experimental objects are also fitted with german silver top-pieces, which may be screwed on to M_3. They are thus easily attached to and detached from the carrier. At convenient heights the brass tube is provided with the following parts: the springs R_1 and R_2 which guide the motion, the marks M_4 for the purpose of reading the position of the carrier, a stopping ring B_3 for confining the motion between the pins, the electromagnetic coil M_5 moving with the carrier, the carriers F_1 of the floats and a scale M_1. As regards these various parts the following may be added.

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[1]) The german silver tube might without disadvantage have been replaced by a simpler arrangement; in the design experiments were contemplated which were not carried out. If due care is taken, the stopping pins may also be dispensed with.

c. Vertical guidance of the carrier. The space between the experimental objects and the inner wall of the vacuum-glass can sometimes not be more than a few tenths of a millimetre when measurements with strong fields are to be made; with the slightest movement of the axis of the carrier from its original position owing to a small asymmetry in the action of the electromagnet or any other cause the carrier would not be able to move up and down freely. This difficulty was quite satisfactorily overcome by guiding the carrier in its up and down motion by the aid of two flattened spiral springs [1]). The outer end of both is fastened to the stationary part of the apparatus, the inner end to the carrier and the plane of the springs is placed at right angles to the axis of the carrier. By the device of using flat springs a movement of the middle in the plane of each of the spirals is almost completely prevented. Usually the upper spring R_1 attached to the carrier remains the same, while each separate experimental object is provided with its own spring, which is removed from the apparatus with the object.

d. The hydrometric equilibrium. To keep the carrier afloat on mercury the upper chamber of the apparatus is provided with a ring-shaped trough Q (in our experiments of glass, later on of china) which is centred on the axis of the carrier. The latter is fitted with a horizontal arm F_1, in which at both ends are fixed the tubes of the floats F_2, glass bulbs, the shape of which is not unlike a flattened ellipsoid. The tubes of these bulbs which are of *very small section* are the only part that projects above the mercury. The section has to be small in order that the upward pressure of the mercury shall vary very little, if the apparatus is to be sensitive to a very small change of the vertical force acting on it. But the size cannot fall below a certain limit, because the tubes must also serve to compensate the diminution in upward pressure in the bath on the experimental object, owing to evaporation.

This compensation is effected by raising the level of the mercury. For this purpose use is made of a plunger D_1, a small glass flask of a shape corresponding to that of the trough which is moved up and down by means of a rod D_2 with thread and milled head D_4 passing through a stuffing box D_3. This contrivance, which was found

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[1]) Springs of that kind are made by cutting on the lathe a spiral groove 0.2 to 0.3 m.m. wide in a plate of german silver (comp. perspective figures $R_1 R_2$). By giving different widths to the spiral strip for a given diameter springs may be obtained of any desired degree of sensibility. The inner end is soldered to a small tube, the outer end is fixed in a clamping screw.

very serviceable supplies the advantage that at the beginning the hydrostatic pressure of the bath need only be approximately compensated, which is done by placing a weight about equal to the pressure on the scale M_1; the accurate adjustment is made afterwards by regulating the level of the mercury.

e. The electromagnetic compensation. The fixed coil N_1 consists of 1275 turns of insulated copper wire, wound on a brass frame, sliding closely over the outside of the enclosure; the coil rests on the ring N_2 and is fixed at the top by the screw N_3. The movable coil M_5 has on the one hand to be as light as possible, on the other it has to produce as great a force as possible; account was therefore taken of the fact that for a given weight it is an advantage to make the radius of the coil large and the number of turns small. The coil contains 248 turns ($d = 0.7$ mm.) in two layers, wound on a thin-walled ebonite tube, which is held between two supporting brass rings $M_6 M_7$ in the shape of wheels, which may be clamped to the carrier at the desired height.

The wire which carries the current to the movable coil passes through and is insulated from the cover G_1 and is connected to the clamping screw G_2 of the upper spiral spring; the current passes through this spring to the ring by which it is attached and which is insulated with ebonite, along the wire G_3 to the coil and back through the carrier itself, the rod of the floats, a platinum wire dipping in the mercury, the mercury and finally a second platinum wire, which carries the current to the cover.

The electromagnetic system is calibrated once for all by fixing to the lower end instead of the experimental object a small scale, on which definite weights are placed, and regulating the current until the balance is obtained.

The level at which the carrier floats, is read on a glass plate M_4 with a scale division in tenths of a millimetre, which is focussed with a microscope L_1 magnifying about 40 times. For this purpose a window of thick plane-parallel glass is sealed on to an opening in the glass tube A_7. On the side opposite to the microscope behind the tube an electric glowlamp is placed in such a position that the scale divisions are seen light on a half-dark background: in this manner it may be very sharply determined when the cross fibre of the microscope exactly coincides with the division.

§ 4. *The experimental tubes.* The substances investigated by us (salts, powdered metal) are all enclosed in glass tubes, concerning which the following may be mentioned.

It is desirable, that the upward pressure due to the bath changes as little as possible when the liquid level falls through evaporation; for this reason the tubes end at the top in thin glass rods M_8 of 2to 2.5 mm. diameter. The lower spiral spring R_2 and the thread by means of which the tube is screwed to the carrier are sealed to this rod with some KHOTINSKY glue. As regards the shape of the tube we have used different forms. Tubes as shown at S_1 are used for substances of high susceptibility, for which the magnetic action on the glass or on the bath plays a subordinate part, so that for them it may be entirely neglected or else a correction may be easily applied. The tube is filled with the substance, when it is still open, at the bottom putting in small quantities at the time, which are evenly compressed in order to obtain a tight filling and at the same time a uniform density throughout the whole tube; the substance is then closed in with a small plug of glass wool to prevent its being heated during the sealing of the tube and the tube is sealed off at the air-pump. The smaller the susceptibility of the substance the greater influence the susceptibility of the air would have and the morene cessary it is to be assured of a good vacuum; a high vacuum, however, is obviously unnecessary.

In cases where account has to be taken of the susceptibility of the glass, which may give rise to fairly strong forces [1]), tubes of type S_2 are used, the lower half of which, separated from the upper half by a glass partition, is exhausted. When this partition is placed on the level of the axis of the poles, the correction for the glass disappears, as it is divided symmetrically with respect to the axis; the susceptibility of the substance is in that case directly compared with that of the vacuum. Type S_3, which does not require further explanation is meant for the measurement of the susceptibility of the liquid in the bath.

§ 5. *Additional apparatus.* The electromagnet is a copy of WEISS's electromagnet which was used in previous researches of this series. The yoke is, however, placed horizontally this time, in order to leave the space below the apparatus completely free (comp. perspective drawing). Usually poles were used of the shape shown, the flat end-faces of which had a diameter of 40 mms. At a polar distance of 15 to 20 mms. the topographical inequality of the field about the middle of the interferrum was not above 0.1 °/₀ within a

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[1]) The susceptibility of glass at low temperature was determined by us in Comm. No. 124*a*, p. 6.

distance of 1 cm. The field-strengths were measured with a Cotton-balance of the usual pattern by W. C. Weber of Zürich.

The circuits of the fixed and movable coils are entirely independent of each other: each of them contains an accurate ammeter, a commutator and rheostats, in which the current is reversed on commutation, in order to neutralise any magnetic influence on the ammeters. They are within reach of the observer seated in front of the microscope.

The field-strength of the electromagnet is given by the current flowing through it; the field was not adjusted until the magnetising current had been several times reversed.

If the evaporation of the bath in the apparatus as described is too strong, as is the case when liquid hydrogen is used, it is diminished by surrounding the bottom half of the vacuum-glass with a vacuum-glass with liquid air.

§ 6. *Method of observation.* Passing by certain simplifications which were often possible we proceeded as follows.

The enclosure and the carrier (without experimental tube) are first adjusted so that the common axis is vertical and passes through the centre of the interferrum. When this position is arrived at, the apparatus is not moved sideways any more.

The experimental tube is then screwed to the carrier and its spring clamped. By means of the weight on scale M_1 the carrier is made to float on the mercury approximately at the desired level and care is taken that the movable coil has the correct position relatively to the fixed coil. The apparatus as a whole is then moved in a vertical direction until the lower end of the experimental cylinder falls about in the line of the axis of the poles, after which the cylinder is adjusted more accurately by turning the apparatus about the ball socket C_1. When finally the poles have been brought at the right distance, everything is ready for the observations at ordinary temperature.

In changing to low temperatures as much weight is added to the scale as agrees approximately with the upward pressure of the bath to be expected and the cover is fastened to the apparatus air-tight by means of the india-rubber ring; after drawing out the poles, the vacuum-glass is placed carefully round the experimental tube, connected airtight and centred in a manner similar to that used in the apparatus of Weiss and Kamerlingh Onnes. After having made sure that everything is airtight, the liquid gas is admitted to the vacuum-glass, the poles are brought back to their position, and the carrier is adjusted to its zero by means of the plunger; the currents in the large electromagnet i_e and in the fixed coil i_f are adjusted to suitable whole numbers and the current i_m (in the movable coil) regulated by a gradual change of the resistance until the carrier has come back to the zero. The current i_m is then noted down and the operations are repeated for the 4 possible combinations of the currents i_e, i_f and i_n. Before and after each observation the zero-position of the carrier is observed or again adjusted; when the change amounts to only a few tenths of a millimetre, there is no objection to do this, more simply than by means of the plunger, by shifting the microscope a little.

(*To be continued*).

Chemistry. — "*The application of the theory of allotropy to electromotive equilibria.*" By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS.)

1. I communicated already before[1]) that the investigation for testing the theory of allotropy with different elements and anorganic as well as organic compounds was in progress. The investigation of the metals, which had been started with *tin* and *mercury*, was somewhat delayed, because all the time had to be devoted to the study of *phosphorus* and *mercury-iodide*, so that only comparatively shortly ago the metals could be taken in hand again.

As may be supposed as known, the theory of allotropy rests on this *fundamental assumption* that every phase of a system that behaves as a unary one is at the least built up of two kinds of molecules which are in internal equilibrium, and must necessarily be taken as the components of a pseudo-system. This theory comprises, therefore, all possible states of aggregation of a substance, and on account of the importance of its conclusions its principial interest lies in the region that has been least investigated up to now, viz. that of the solid state.

Now it is clear that the experiments which are carried out to test this theory are undertaken in the first place to prove that the different states of aggregation and particularly the solid phases of a substance which presents the phenomenon of allotropy, are really mixtures, and in internal equilibrium, for every time that this succeeds a confirmation of the said theory has been found. In the second place an attempt may be made by a continuation of the in-

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[1]) These Proceedings, April 26, 1912, XIV, p. 1199.

vestigation to find something about the type of the pseudo-system, which is, of course, a far more difficult problem.

2. The test may now take place in different ways:

a. by an inquiry into the influence of the previous treatment on the point of solidification, resp. melting point, point of transition etc.

b. by an inquiry into the influence of the previous treatment on the solubility.

c. by an inquiry into the influence of the previous treatment on the specific gravity, the viscosity, the index of refraction, the specific heat, and further on every other property of the substance.

d. by the study of any temperature function, in which a confirmation of the said theory may follow from the way in which this function varies with temperature.

Besides in this way the theory of allotropy can probably also be tested in another way, by the fact that as I observed already before¹) it may be expected that the different kinds of molecules of a same substance will in general differ in reactive power.

On that occasion I already pointed out that by means of this the passivity of the metals might be explained, hence also the permanent or periodic changes in the potential difference between metal and electrolyte, in the solution of some metals by an electrolytic way, so that when this view should prove correct, a new means would have been found to prove the complexity of the metals in the study of the phenomenon of passivity brought about by a purely chemical or by an electrolytic way.

As I am of opinion that the experiment really shows the validity of the above mentioned supposition, I will expound here further how the electrolytic deposition and solution of metals must be considered in the light of the theory of allotropy, and at what conclusions we then arrive.

3. When we have a metal that shows the phenomenon of allotropy, different kinds of molecules will be present in this metal. To simplify the matter as much as possible, let us assume that molecules M_2 occur by the side of mon-atomic molecules M. When this metal is immersed in an electrolyte and emits ions, two different kinds of ions will be emitted; if the metal as ion, carries three positive charges per atom they will be the ions $M^{\cdot\cdot\cdot}$ and $M_2^{\vdots\vdots\vdots}$ on the supposition made.

Up to now it has always been assumed that a metal emits only one kind of ions, now the theory, however, states that when one of the coexisting phases is in internal equilibrium, the other must

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¹) These Proceedings, May 31, 1913, XVI, p. 191.

also be in internal equilibrium, so that when in the metal the molecules M and M_2 are in equilibrium, there will be equilibrium between the ions $M^{\cdot\cdot\cdot}$ and $M_2^{\cdot\cdot\cdot\cdot\cdot\cdot}$ in the electrolyte. So the simplest assumption is this that the different ions are emitted by the metal, though this need not take place in the ratio in which they are present as molecules in the metal. In this way we then arrive at the result that the unary electromotive equilibrium may be considered as a special equilibrium in the series of electromotive equilibria of homogeneous mixed crystals, which we may imagine as being built up of the molecules M and M_2 in different ratio.

Let us now suppose that fig. 1 [1] for a definite T,P and a definite total metal-ion concentration indicates the potential difference Δ between electrolyte and metal as function of the concentration.

The point a denotes the potential of a solution of an M-salt of definite metal-ion concentration containing exclusively $M^{\cdot\cdot\cdot}$-ions, with

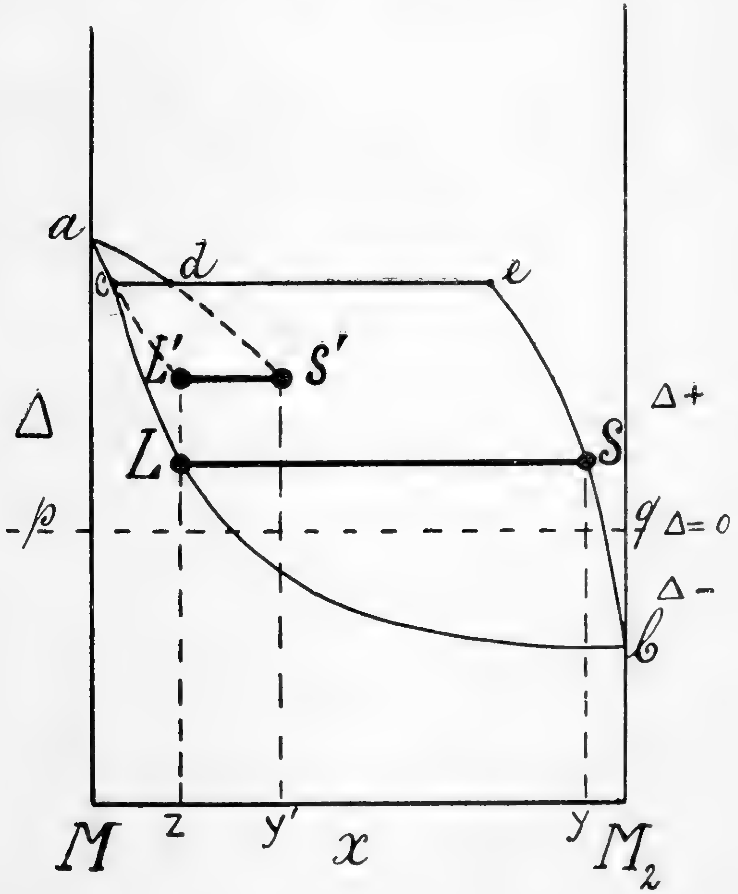

Fig. 1.

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[1] Cf. **Reinders**. Zeitschr. f. Phys. Chem. 42, 225 (1902).

regard to a metal merged in this solution, which is thought to be entirely built up of M-molecules.

The point b denotes the same thing for a solution of the same metal-ion concentration as the just-mentioned solution, but containing exclusively $M_2^{\because\because}$-ions, a metal being immersed in this solution which consists exclusively of M_2-molecules. The metal M is here supposed to be a base state, and M_2 to be a noble state of the same metal.

Now it has been assumed in fig 1 that the metals M and M_2 are miscible to a limited degree in the solid state with the assumed T and P. The two branches of the interrupted series of mixing are indicated by the lines *ad* and *eb*, the solutions which can be in electromotive equilibrium with these metal phases being indicated by *ac* and *cb*. The line *cde* denotes the three-phase electromotive equilibrium. In general this three-phase equilibrium can also lie above the potential difference of the two metals, but this case is not considered here, because we shall no doubt always have to do with association in metals, in which it is to be expected that the metal phase will contain more of the most composite pseudo-component than the coexisting solution.

The phases coexisting in case of electromotive equilibrium of course lie on a horizontal line, which, the Δ, x-figure being given, and the potential difference being known, immediately enables us to know the concentration of the coexisting phases.

Now we may of course apply VAN LAAR's [1]) formula for the potential difference between mixed crystals of two metals and electrolyte also to the case supposed here. Considering that for electromotive equilibrium

$$\Delta = -\frac{\overset{+}{\mu}_M - \mu_M}{v_M \varepsilon} = -\frac{\overset{+}{\mu}_{M_2} - \mu_{M_2}}{v_M \varepsilon} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $\overset{+}{\mu}_M$ and $\overset{+}{\mu}_{M_2}$ are the mol.-potentials of the $M^{\cdots}$ and $M_2^{\because\because}$ ions in the electrolyte, and μ_M and μ_{M_2} those of the molecules M and M_2 in the metal, v_M and v_{M_2} representing the number of charges of the different metal-ions, we arrive at the following relation for the potential difference

$$\Delta = \frac{RT}{v_M \varepsilon} ln \frac{K_M(1-x)}{C_M} = \frac{RT}{v_{M_2} \varepsilon} ln \frac{K_{M_2} x}{C_M^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It follows from this formula, in which as I showed before, K_M

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[1]) Chem. Weekbl. **41**, 1905.
Lehrbuch der Theoretischen Elektrochemie.

and K_{M_2} indicate the saturation concentrations of the metal-ions $M^{\cdot\cdot\cdot}$ and $M_2^{\cdot\cdot\cdot\cdot\cdot\cdot}$ 1), that

$$\left(\frac{K_M(1-x)}{C_M}\right)^{\frac{1}{\nu_M}} = \left(\frac{K_{M_2}x}{C_{M_2}}\right)^{\frac{1}{\nu_{M_2}}} \quad \ldots\ldots \quad (3)$$

and as in the case supposed here

$$\nu_{M_2} = 2\nu_M \quad \ldots\ldots \quad (4)$$

we get:

$$K^2{}_M \frac{(1-x)^2}{x} = K_{M_2} \frac{C^2{}_M}{C_{M_2}} \quad \ldots\ldots \quad (5)$$

4. The Δ, x figure 1, drawn here, holds for the case that the two kinds of molecules and the two kinds of ions *cannot* be converted into each other. If, however, an internal equilibrium is established, only electromotive equilibrium is possible, when the coexisting phases are both in internal equilibrium. This is immediately seen in the following way. Equation 1 runs

$$\frac{\overset{+}{\mu}_M - \mu_M}{\nu_M \varepsilon} = \frac{\overset{+}{\mu}_{M_2} - \mu_{M_2}}{\nu_{M_2} \varepsilon}.$$

Now

$$\nu_{M_2} = 2\nu_M$$

so that

$$2\overset{+}{\mu}_M - 2\mu_M = \overset{+}{\mu}_{M_2} - \mu_{M_2}$$

or

$$2\overset{+}{\mu}_M - \overset{+}{\mu}_{M_2} = 2\mu_M - \mu_{M_2} \quad \ldots\ldots \quad (6)$$

from which follows that when in case of electromotive equilibrium internal equilibrium prevails in the electrolyte between the metal-ions, for which:

$$2\overset{+}{\mu}_M = \overset{+}{\mu}_{M_2},$$

a consequence of this is that:

$$2\mu_M = \mu_{M_2},$$

or in words that internal equilibrium must then also prevail in the metal, and vice versa. As is directly to be seen, the same conclusion follows from equation (5), when we assume the validity of the law of the chemical mass-action also in this case. As said before the Δ,x-figure holds for a definite T, P and total metal-ion concentration.

The internal equilibrium in the metal phase is perfectly defined for definite T and P. The internal metal-ion equilibrium in the

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1) These Proc. May 9 1906. IX p. 2.

electrolyte, however, is dependent on the concentration; C_M resp. C_{M_2} varies with the total concentration, and together with it according to equation (2) also the potential difference Δ. If, therefore, also the total metal-ion concentration has been fixed, everything is perfectly determinate.

Let us put that for given T, P and total metal-ion concentration, for which our Fig. 1 holds, the internal equilibrium between the metal-ions is indicated by the point Z, it follows from the Δ, x-figure that for unary electromotive equilibrium the solution L will coexist with the metal phase S for a potential difference indicated by the situation of the line LS. It has been said that the internal equilibrium in the metal phase is solely determined by T and P, i.e. the point y, but the situation of S in the Δ, x-figure depends of course on the total metal-ion concentration in the electrolyte.

We see, however, that when we prolong the lines *ac* and *ad* metastable, the same solution Z can be in unary electromotive equilibrium with another metal phase for a higher potential difference, viz. with the phase S'. This second unary electromotive equilibrium is, however, metastable, whereas the first is stable.

If we first of all assume that we have *always* to do with internal equilibrium we may question what will happen when the solution Z is electrolysed, while the total metal-ion concentration is kept constant. It is clear that for the separation of a metal phase, in which another internal equilibrium prevails than in the electrolyte, a molecular transformation will be necessary, which in our case consists of the reaction $2M \rightarrow M_2$. We now see from Fig. 1 that the metastable phase S' lies much closer to the liquid L' than the stable phase S to the liquid phase L. *It follows from this that the deposition of the metastable metal S' requires a much smaller internal transformation than that of S, and the consequence of this will be that when electrolytic metal depositions is carried out at temperatures at which the velocity of transformation of the metastable modification to the stable modification is small, the metastable state is deposited.*

It is, therefore, seen from this that for so far as OSTWALD's "*Gesetz der Umwandlungsstufen*" holds also here, the explanation is quite analogous to that given by me for the succession in the appearance of different allotropic states of the same substance in the cases in which the deposition was not effected by the supply of electric energy [1]). On that occasion I already pointed out that OSTWALD's rule

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[1]) Zeitschr. f. phys. Chem. **84**, 385 (1913).

need not necessarily *always* be valid, and here too exceptions may be expected, when viz. the metastable and stable solid phases differ only little in concentration.

5. We have discussed the phenomenon of electrolysis here on the supposition that the internal equilibrium in both phases sets in with so great a velocity that at any moment internal equilibrium prevails, but this is a limiting case, and it is certain that the setting in of the internal equilibrium at least at the ordinary temperature, requires an appreciable space of time. It is therefore of importance to ascertain what the phenomena will be when the setting in of the internal equilibrium cannot keep pace with the changes of concentration caused by the electrolytic process.

For this purpose it is simplest first of all to assume the other limiting case; viz. that the internal transformations are *entirely* wanting during the experiment. We think two rods of the same metal M, which have somehow assumed internal equilibrium at the temperature and the pressure for which Fig. 1 holds. These rods are used as electrodes, and placed in some salt solution of the same metal, and of a concentration, for which Fig. 1 also holds. Suppose internal equilibrium also to exist in the solution, then both metal electrodes are in electromotive equilibrium with the solution and the coexisting phases are indicated in Fig. 1 by the points S and L. Then we think a negative catalyst to be added, after which there can be no question any more of the setting in of internal equilibrium.

Fig. 2 represents the potential differences, which exist between the two electrodes and the electrolyte. The distance $cb = de$ indicates

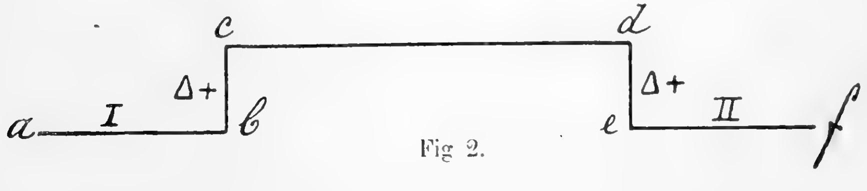

Fig 2.

the potential of the solution with respect to the metal electrodes. So the situation of cd agrees with the potential of the electrolyte, and that of the lines ab and ef with the potentials of the two metal electrodes I and II. So the potential of the electrolyte is here positive with respect to that of the metal electrodes.

Let us now connect the two metal electrodes with the poles of a battery; let us put I to be the positive, and II the negative pole, then electrode I will be dissolved, whereas metal from the electrolyte deposits on the electrode II. If we again imagine the total metal ion concentration kept artificially constant, Fig. I can account to us for what will happen.

If positive electricity is applied to electrode I, the electromotive equilibrium is broken for a moment, and a new electromotive equilibrium sets in, in consequence of molecules of the metal I being dissolved as positive ions. If the ions $M^{\cdot\cdot\cdot}$ and $M_2^{:::}$ entered the solution in *the same* ratio as they were present as molecules in the metal, the composition of the metal would *not* change while the electrolyte gets richer in $M_2^{:::}$-ions. It is clear that as we now exclude internal transformations, in this way there cannot be question any more of a renewed setting in of the electromotive equilibrium. If the metal-ions entered the solution exactly in the same ratio in which they are already present in the electrolyte, the concentration of the metal phase would change, whereas that of the electrolyte remained the same, which could not lead to a renewed setting in of the electromotive equilibrium either.

Thus we see that the metal phase will emit $M^{\cdot\cdot\cdot}$ and $M_2^{:::}$-ions in a ratio lying between L and S, in consequence of which both phases become richer in M_2, and two phases can therefore form again, which can be in electromotive equilibrium with each other. On supply of positive electricity to the electrode I the potential difference Δ will, therefore, have to *descend*, and when the dotted line pq in Fig. 1 indicates the potential difference *zero*, it is even possible that the potential difference Δ at electrode I becomes *negative*.

What will take place at the other electrode II? At this electrode metal will be deposited, and it is easy to see that assuming that at first the stable phase S separates, the different metal-ions will be discharged in a ratio lying between L and S, because only in this way a renewed setting in of the electromotive equilibrium is possible. Hence the coexisting phases will become richer in M on the side of the metal-deposition, and the potential difference will become *greater* positive. For a definite potential difference indicated by the line ce another metal phase d will arise by the side of the metal phase e, and when the electric current continues to pass through, the potential difference remains constant till the metal ions in the electrolyte depositing on the metal phase e, have converted this latter phase, at least superficially, into the metal phase d. Then the potential difference can increase again, and the metal phase moves along the line da and the electrolyte along ca.

So we may conclude from the foregoing that when the current has continued to pass for some time, figure 2 of the potential differences may have been changed into figure 3.

Though at first there did not exist a potential difference between I and II, this will, indeed, be the case after some time, because in consequence of the electrolytic process, one metal electrode has become less base or even noble, whereas on the other hand the other electrode has become baser.

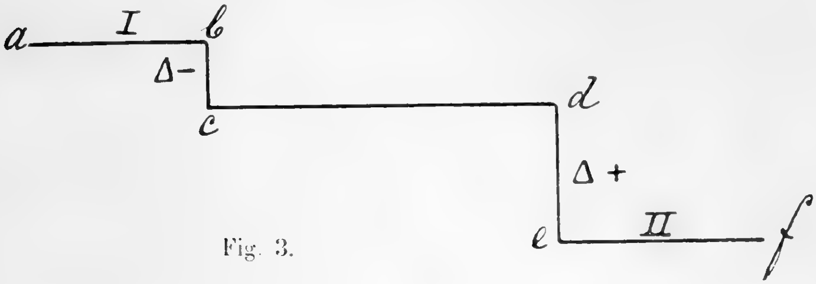

Fig. 3.

As has been said, in many cases the *metastable* state will separate, and then *part* of the potential difference is, of course, to be attributed to this. This, however, does not affect the nature of the phenomenon.

6. Here, however, the limiting case has been assumed that the metal molecules and ions are not transformed into each other at all during the experiment, which, however, will not be the case in general. As a rule the system will not entirely behave as a unary one with regard to the metal molecules and ions, nor will it behave entirely as a pseudo-system, and for this very reason exceedingly remarkable phenomena may present themselves. Thus it has been found that in some cases periodic oscillations occur in the potential difference in the above described experiment, which, as I stated before, seems to indicate that the internal transformations at first are slackened by negative catalytic influences, which however, after a certain degree of metastability has been reached, are no longer able to maintain the formed metastable state, so that all at once an internal transformation may set in, which propagates with great rapidity all over the metastable metal surface. When this transformation, in which internal equilibrium has been more or less approached, has taken place, the same phenomenon may repeat itself. I have already pointed out that the negative catalytic influence is probably exerted here by a trace of oxygen dissolved in the metal, which influence can, of course, also be active when no periodic oscillations in the potential difference occur, but a continuous change in the same direction.

In this connection it may be pointed out that *explosive antimony* is probably a metal phase which is far removed from the state of internal equilibrium, and in which the internal transformations are impeded by the dissolved antimony-chloride.

7. In connection with the foregoing it is desirable to draw attention to this that according to these considerations *the contact with the solution of a salt of the metal must have an accelerating influence on the setting in of the internal equilibrium of the metal.*

In general we shall namely be no doubt justified in assuming that the internal metal-ion equilibrium establishes itself pretty rapidly in the electrolyte at the ordinary temperature and pressure, whereas under the same circumstances the metal probably will not get in equilibrium or exceedingly slowly. If we imagine the case that at the ordinary temperature and pressure a metal is immersed into the solution of a salt of this metal, then, assuming the same case as represented in figure 1, the metal will contain too many molecules M or too many molecules M_2. The electrolyte, which indeed is thought to be in internal equilibrium cannot be in electromotive equilibrium with this metal, and the consequence of this is that both the electrolyte and the metal will tend to reach this electromotive equilibrium. Put that the metal contains too many M molecules, then $M_2^{\cdot\cdot\cdot}$ ions will deposit from the electrolyte on the metal, and M molecules will be sent as ions in solution by the metal. In the electrolyte the ion concentration now remains constant in consequence of internal transformations, but the concentration in the surface of the metal changes in such a way that it finally agrees with the internal equilibrium. So the surface of the metal has reached internal equilibrium by means of the electrolyte, and now the possibility is given that also the layers that lie deeper will assume internal equilibrium by self-grafting.

If the temperature is that of the transition point, the electrolyte lies exactly in c (Fig. 1) with internal equilibrium, and above this temperature on the line ac. At the point of transition the electrolyte will greatly promote the internal equilibrium both in the metal phase e, and in the metal phase d for the just-mentioned reasons.

8. In conclusion I will direct attention to another circumstance which may be expected with great probability on the ground of the considerations of the theory of allotropy.

If for the sake of simplicity we retain the case of a metal consisting of molecules M and M_2, then it is clear that as we have assigned *three* positive charges to every atom as ion, the molecules $M\,Cl_3$ and $M_2\,Cl_6$ will be formed on solution of this metal in hydrochloric acid. The solid salt which may be separated from this solution will also contain both kinds of molecules, and in the state of internal equilibrium in a ratio which is entirely determined by T and P. Let us now suppose that this salt is reduced with hydrogen at a temperature as low as possible, then when the temperature is too low for the setting in of the internal equilibrium of the molecules M and M_2, a metal will form, which as far as internal concentration is concerned, may differ very much from the metal as we know it. If the obtained metal relatively contains more simple molecules than in the state of internal equilibrium, it will contain a greater reactive power, because probably an association will be generally attended with a decrease of chemical activity.

In this way perhaps the pyrophoric phenomenon will have to be explained, which has already been observed for different metals, and which disappears again when the metal is heated at higher temperature.

I have now briefly indicated the different directions in which for some time the metals have been studied in my laboratory.

SUMMARY.

In this paper the theory of allotropy was applied to the electromotive equilibrium between metal and electrolyte, in which it appeared that a metal exhibiting the phenomenon of allotropy, and consequently composed of different kinds of molecules (different in degree of association), immersed in an electrolyte, will emit different kinds of ions. By means of this it could be demonstrated that the unary electromotive equilibrium belongs to the Δ,x-figure of a pseudo-system, which system might be realized for the case that the different kinds of metal molecules and ions could not be transformed into each other e.g. by the presence of a negative catalyst.

The application of this new view to the phenomenon of electrolysis led to the following results.

In the first place it could be made clear that and why with electrolytic metal deposition in many cases *not the stable but the metastable* phase will be obtained. In the second place the theory showed that when the internal transformations under negative catalytic influences fail to appear or are impeded, the metal that is made to dissolve by an electrolytic way, will get *nobler* superficially [1]), whereas the newly deposited metal will be *baser* [2]) than what went into solution.

In the third place it was made probable that also the periodic oscillations in the potential difference, which point to a periodic enobling of the metal surface may be accounted for from the same point of view.

In the fourth place it was demonstrated why the contact of a metal with the solution of one of its salts must exert an accelerating influence on the setting in of the internal equilibrium of the metal.

Finally attention was drawn to the possibility that on reduction of metal compounds at low temperatures metal masses are obtained which are far from the state of internal equilibrium, and can exhibit an abnormally great chemical activity. This will be the case when they differ from the ordinary metal states by a greater content of the more simply composed kinds of molecules. The pyrophoric states observed for some metals are possibly to be explained in this way.

Anorg. chemic. laboratory
Amsterdam, Dec. 20, 1913. *of the University.*

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[1]) This may also mean: becomes less base.
[2]) „ „ „ „ : „ „ noble.

(January 29, 1914).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday January 31, 1914.
Vol. XVI.

President: Prof. H. A. Lorentz.
Secretary: Prof. P. Zeeman.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 31 Januari 1914, Dl. XXII).

CONTENTS.

Chemistry. — *"Pseudoternary systems of acid anhydrides and water. I. Phthalic anhydride."* By Dr. H. R. Kruyt. (Communicated by Prof. Ernst Cohen).

(Communicated in the meeting of December 27, 1913).

For reasons, which will be further explained in a following treatise of this series, the knowledge of the heterogeneous equilibria in systems of acid anhydrides and water seemed to me of importance. The only quantitative investigation that has been made on this subject is found in the dissertation of E. van de Stadt [1]) and relates to phthalic- and succinic anhydride. The results thereof may be summarised as follows: If we shake the acid with water at a definite temperature we soon attain an equilibrium; if, however, we shake the anhydride with water, we notice a continuous rise of the total-solubility [2]) at which values are attained far above the solubility of the acid; then follows a period of fall quite as regular as the previous rise, no discontinuity occurs in this process; finally we again arrive, at the solubility of the acid. These results suggest the following interpretation: the anhydride has a greater solubility than the acid, hence occurs the provisional high total concentration, but

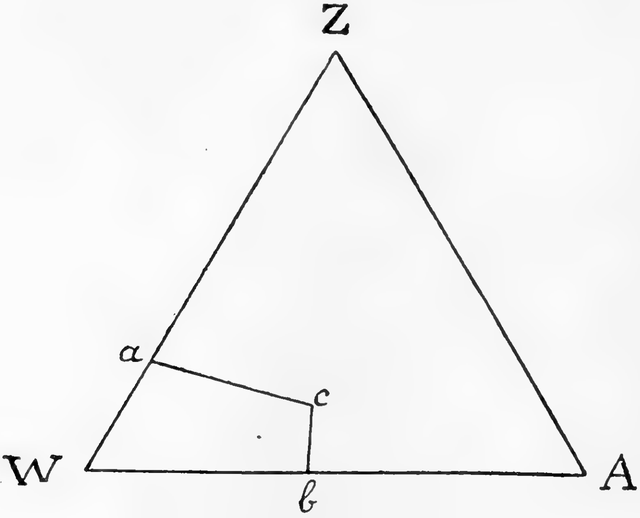

Fig. 1.

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[1]) Amsterdam 1901. Also Zeitschr. f. physik. Chem. **31**, 250 (1899) and **41**, 353 (1902).

[2]) By this is meant the acid concentration as found by titration which represents the sum of the acid- and anhydride molecules.

gradually the anhydride disappears by conversion into the acid and so we again finish with the acid-solubility.

This explanation, however cannot be satisfactory, for it is assumed herein that the phase equilibria set in while the reaction equilibrium is modifying the condition in the homogeneous solution. Thus we have a pseudoternary system: water-anhydride-acid (W-A-Z). In fig. 1 has been drawn the solubility-isotherm, the equilibrium line will about coincide with the axis WZ. The position of a and b is given by the assumed difference in solubility between the acid and the anhydride. If now we shake water and anhydride the solution will about follow the lines Wb and bc; in c the solubility of the phthalic acid has been attained and if then a fall occurs in the total solubility this means to say that *solid phthalic acid* has deposited. But then the equilibrium is non-variant (p,t) and hence a fall cannot take place immediately after a rise; no continuous maximum can follow, but a long stop at the highest concentration must occur. Now this was not observed by VAN DE STADT; on repeating the experiment at 20° I also noticed that the concentration of a solution when shaken with phthalic anhydride in a rotating flask did not come to a standstill, but passed continuously through a maximum value.

In Table I this frequently repeated experiment is indicated. $N/10$ sodium hydroxide was used for the titration with phenolphthalein as indicator.

TABLE I.

3.17 gr. Phtalicanhydride + 90 cc. water.

No.	Time	Concentration in millimols per L.
1	¼ hour	17.5
2	½ »	34.4
3	¾ »	55.1
4	1¼ »	46.2
5	1½ "	41.3
6	4 »	36.4

The solubility of phthalic acid is 35.2 millimols p. litre; it was always attained the next day.

It should be noticed that in the interval between experiments 3 and 4 a finely divided solid mass had deposited (which very much impedes the filtration through cotton wool); indeed the experiments following have really been carried out with the two solid phases, anhydride and acid; even after experiment 6 a few long needles of anhydride were still readily visible.

Afterwards the shaking bottle was provided with acid as well as with anhydride so as to determine the position of point *c*. Now indeed a composition was attained that remained fairly constant for a longer time (see the first two columns of table II). But it seems peculiar that 1. the value found lies but little above the solubility of the phthalic acid and 2. that the value was found to differ in different experimental series. In the dissertation of VAN DE STADT we also find in the second table on page 49 an extremely smooth maximum as the progress of the solubility in the presence of the two solid phases.

Perhaps an explanation may be found here owing to a peculiar relation between the velocities of attainment of the homogeneous and heterogeneous equilibria. As this necessitates the knowledge of the proportion of anhydride to acid in the various solutions this proportion was determined. The chemical method applied by LUMIÈRE and BARBIER [1]) in the study of the equilibrium in the homogeneous system acetic-anhydride-water proved impracticable here, but the electric conductivity power previously applied by VOERMAN [2]) and by RIVETT and SIDGWICK [3]) in the study of the progressive change of the reaction in homogeneous systems, seemed to furnish a better method.[4])

In order to render unnecessary the repeated withdrawal of large volumes of liquid a small plunging electrode was constructed with a capacity that just required suitable resistances for liquids used in these experiments.

We made use of DE HAEN's phthalic anhydride (m.p. 130°.6 in VAN EIJK's apparatus); phthalic acid was prepared from that anhydride by complete hydratation; titre and conductivity power of the saturated solution appeared to be independent of the quantity of solid phase, hence foreign substances were absent. By numerous determinations with concordant results we found for the solution saturated with phthalic acid:

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[1]) Bull. Soc. Chem. de France [3] **33**, 783 (1905).

[2]) Diss. Groningen 1903, Rec. d. Trav. Chim. d. Pays-Bas **23**, 265 (1904).

[3]) Journ. Chem. Soc. **97**, 732 and 1677 (1910).

[4]) The method also has been applied by BOËSEKEN and his collaborators, cf. Rec. d. Trav. Chim. d. Pays-Bas 1912 and these Proceedings. (Note added in the English translation).

35.2 millimol. p. litre spec. cond. power **0.001952**.

If we take μ_∞ for 20° on 0.333, OSTWALD's law of dilution then yields $k = 0.117$, which result was put to the test in a number of solutions. The acid concentration may now be calculated from the specific conductivity power[1]).

The experiments were carried out by rotating a small flask in the usual manner in a thermostat. The conductivity vessel was furnished with a trebly perforated stopper. Through the stopper was put the plunging electrode, also a little tube leading to the cotton-wool filter and another one to which suction could be applied. Immediately after 11 cc. of the liquid had been withdrawn the resistance was measured in the usual manner (WHEATSTONE bridge, alternating current and telephone); 10 cc. were then pipetted off and titrated.

In Table 2 is found the complete composition of the solutions which are shaken with the two solid phases. We notice that although a totally stationary maximum value was not found, it is very surprising to find how remarkably little anhydride is contained in the solutions which during about two hours still change but little in composition.

TABLE II.

2.05 gr. acid + 2.72 gr. anhydride + 90 cc. water.

Time	Titration	Spec. cond. power	Acid	Anhydride	Maximum average
11 min.	40.0	0.001970	35.8	4.2	
27 »	42.1	2027	37.7	4.4	
65 »	41.1	2002	36.8	4.3	37.0 acid
96 »	41.5	2002	36.8	4.7	4.4 anhydride
147 »	40.7	1995	36.6	4.1	

Hence a large solubility of the anhydride molecules appears but little probable. It is interesting to notice that these solutions contain more phthalic acid than the purely aqueous ones. The solubility of the acid is thus much promoted by the anhydride present.

Fig. 2 appears to be the most appropriate one for expressing these results.

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[1]) As to the neglecting of the influence of the anhydride on the conductivity power see RIVETT and SIDGWICK (l.c.).

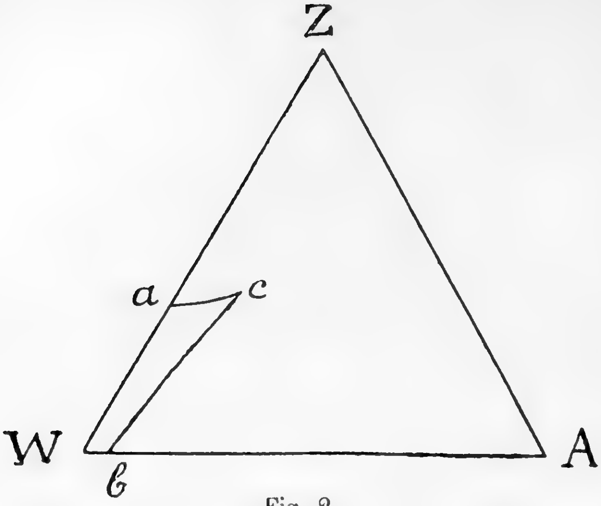

Fig. 2.

a lies at a greater concentration than *b*, the solution *c* contains more acid than *a*. Looking at the presumably very slight solubility of the anhydride and the fairly large reaction velocity of the hydratation (four times greater[1]) than that of acetic and succinic anhydride) it will be understood why in different experimental series were found maximum values which mutually slightly differed. (Some tritration values from different series: 41,4 — 41,4, 44,0 — 44,3 — 44,5). Three processes are taking place continuously: solution of anhydride, hydratation thereof and crystallisation of phthalic acid. The latter will no doubt take place spontaneously as a large quantity of finely divided solid phase is present: the second takes place fairly rapidly and the first is evidently not rapid enough to maintain the condition of the point *c*. That appears from table 3 where this last reaction

TABLE III.

2.25 gr. acid + 4.37 gr. finely powdered anhydride + 90 cc. water.

Time	Titration	Spec. cond. Power	Acid	Anhydride
30 min.	43.7	0.002050	38.5	5.2
60 „	44.5	2056	38.7	5.8
101 „	44.1	2056	38.7	5.4
134 „	42.7	2027	37.7	5.0
222 „	40.8	1986	36.3	4.5

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[1]) Rivett and Sidgwick l.c.

was promoted by adding a large quantity of finely powdered anhydride.

If we compare these results with those of Table 2, we notice that now indeed the anhydride-concentration has risen: as the acid concentration also lies higher this is evidently also promoted by the concentration increase of the other pseudo-component.

It now still remained to be seen whether the internal composition of the liquids which are shaken with anhydride only, agrees with the conclusions drawn from the above experiments.

In Table IV is shown the result of a measurement.

TABLE IV.

3.11 gr. anhydride + 90 cc. water.

Time	Titration	Spec. cond. Power	Acid	Anhydride
25 min.	29.2	0.001663	26.3	2.9
50 »	54.5	2286	47.0	7.5
75 »	47.2	2193	43.6	3.6

From this we notice that the large total-solubility found when shaking with anhydride is mainly an acid-solubility. In another series, for instance, 43.6 acid: 7.7 anhydride was found for the composition at the greatest total solubility. More than the sixth part can therefore never be put to the account of the anhydride. As originally no solid phthalic acid is present as a solid phase we are presumably dealing here with supersaturated solutions, although on the other hand, anhydride and acid seem to promote each others solubility. It is therefore, intelligible that, after the maximum has been attained we can plainly observe the separation of the phthalic acid in the liquid and also that the liquidum phase gets impoverished both in acid and anhydride. As regards the acid this is presumably the case in a much higher degree than indicated in Table 4 as the withdrawal, after the maximum concentration has been passed, always takes a few minutes on account of the clogging of the filter by the deposited exceedingly finely divided phthalic acid. In the meanwhile of course, a little of the anhydride from the clear liquid in the conductivity vessel becomes hydrated again before the measurement could be executed and thus a somewhat too high acid and a somewhat too low anhydride concentration is found.

The progressive change of the solubility is also characterised by the fact that after about 25 minutes, when the solubility of phthalic acid (35.2 millimol. per litre) has not yet been attained, the condition is already such that the solution contains a preponderance of acid. The idea that phthalic anhydride should be readily soluble is, therefore, without any foundation; the anhydride concentration can, moreover, not be calculated by simply deducting the solubility of the acid in water from the total solubility.

This last experimental series therefore also confirms our contention: the anhydride passes into solution as such and then becomes hydrated and this so rapidly in comparison with its solubility velocity that the non-variant (p,t) equilibrium is not attained, or at least not permanently so. The anhydride, if we will not credit it with an *abnormally* small solubility velocity (for which there exists no reason, just the contrary), has a much smaller solubility than the acid.

No measurements have as yet been carried out with succinic anhydride, but looking at the parallel behaviour of the two acid anhydrides similar relations may be expected there also.

Owing to the peculiar relations between the homogeneous and the heterogeneous reaction velocities in this kind of systems, we are here at the limitation where we may still speak of actual pseudo ternary systems. In connection therewith and other correlated questions the investigation of different systems is being continued.

Utrecht, Dec. 1913. VAN 'T HOFF-*Laboratory.*

Chemistry. — *"The mechanism of the acid formation of aliphatic acid anhydrides in an excess of water".* By Prof. J. BÖESEKEN and P. E. VERKADE. (Communicated by Prof. HOLLEMAN).

(Communicated in the meeting of December 27, 1913).

The communication of WILSDON and SIDGWICK [1]) on the hydratation of some acid anhydrides induces us to give a short résumé of the results obtained by us when investigating the hydratation of the aliphatic acid anhydrides.

This investigation [2]) has already been announced by one of us some time ago. He had found that the hydratation constant of the cyclic acid anhydrides was connected with the dissociation constant of the acids formed thereof. As it was his intention to get to know

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[1]) Soc. **103**, 1959 (1913).

[2]) Recueil **31**, 90 (1912).

something about the ring tension eventually occurring in those acid anhydrides, it had to be decided whether the dissociation constant of the acids was the only or principal factor which, besides that ring tension, could exert an influence on the hydratation velocity. The hydratation of the anhydrides of the fatty acids seemed to him the most appropriate one, because in this the factor of the ring tension is excluded, whilst that of the dissociation constant can be readily applied. Moreover, the values of the dissociation constants of the fatty acids do not diverge much, so that other factors can exert their influence distinctly. While the detailed account of this investigation will be published in another form [1]), we give here a short summary of the results obtained.

The hydratation velocity of the acid anhydrides was determined in the manner indicated by VOERMAN [2]), namely by measuring the conductivity of the aqueous solutions in which it is assumed that only the acid determines the conductivity and that this is not modified by the anhydride still present.

The conductivity of the acids and the dissociation constant to be deduced therefrom had to be accurately known, because from the conductivity found in the hydratation the concentration of the acid formed (and consequently that of the anhydride consumed) had to be calculated. As the values given in the literature for the diss. const. often differ considerably, we judged it necessary to make new determinations thereof.

They were carried out in the usual manner already frequently described by us.

A correction for the conductivity of the water itself ($1-1.5 \times 10^{-6}$) was not applied, because this conductivity is caused in the carefully

Dissociation-constants of the fatty acids.

	μ^0_∞	μ^{25}_∞	$K^0 \times 10^5$	$K^{25} \times 10^5$
acetic acid	—	387	—	1.82
propionic „	241	384	1.37	1.31
n. butyric „	239	381	1.55	1.47
isobutyric „	239	381	1.53	1.44
isopropylacetic acid	—	378	—	1.68

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[1]) Dissertation of P. E. VERKADE to appear shortly.

[2]) Recueil **23**, 265 (1902). Dissertation Groningen 1903.

cleaned Jena vessels by carbon dioxide and the dissociation thereof is practically repelled by the fatty acids.

The constant given above for *iso*propylacetic acid (= 1.68) has been found equal for both the commercial and synthetic product. As the former is contaminated with methylethylacetic acid and as the constant thereof does not differ much from that of the pure *iso*valerianic acid [1]), this was to be expected.

The measurements of the hydratation velocity were executed in the same manner as those described previously. [2]) The anhydride

Propionicanhydride 0°.

t	$\varkappa$	c	$0.4343\,k^{0}$
0	0.0_4598	0.00481	—
3	664	594	0.00689
4	685	631	691
5	705	668	695
6	725	701	686
7	745	740	700
8	764	767	679
9	780	809	699
11	815	879	706
13	844	940	699
15	874	0.01002	698
17	902	1070	708
20	938	1150	698
23	973	1238	704
26	0.0_31008	1325	712
29	1037	1401	712
32	1064	1473	711
36	1098	1563	710
∞	1497	2913	—

mean: $0.4343\,k^{0} = \mathbf{0.00700}$.

Aceticanhydride 25°.0.

t	$\varkappa$	c	$0.4343\,k^{25}$
0	0.0_3132	0.00674	—
1	1555	937	0.0721
1½	164	0.01048	700
2	172	1151	713
2½	1795	1250	718
3	186	1341	718
3½	192	1425	713
4	1965	1486	703
4½	2015	1560	706
5	206	1628	704
5½	2095	1680	703
6½	213	1734	705
∞	2505	2380	—

mean: $0.4343\,k^{25} = \mathbf{0.0709}$.

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[1] Billitzer, Sitz. Ber. Ak. Wien 1899, p. 416.

[2] Rec. **31**, 80 (1912).

was shaken with previously warmed (cooled) conductivity water and then filtered rapidly into the resistance vessel.

As 0-point was taken the moment that the irregular initial reaction was over and the bridge readings could take place accurately.

Subjoined are found some of these measurements. (See p. 720).

In this manner the following constants were obtained for different acid anhydrides.

Hydratation-constants of the fatty anhydrides.

	$0.4343\,k^0$	$0.4343\,k^{25}$	Values found by RIVETT, WILSDON and SIDGWICK.
acetic anhydride	—	0.0713	0.0701
propionic „	0.00700	0.0372	0.0372
n. butyric „	0.00471	0.0243	0.0204
isobutyric „	0.00454	0.0227	
aceticpropionicanhydride	—	0.0522	

This table contains a résumé of the constants obtained at an anhydride concentration of 0.01—0.02 normal. We chose this small concentration, because it had been noticed by SIDGWICK and his coadjutors [1]) that the constant decreases when a much greater concentration is taken and also because the higher fatty acids were soluble to the extent of about 0.03 normal only.

Only under these conditions could the constants obtained be compared mutually.

a. From these data it follows in the first place that the influence of the temperature is about the same for the fatty acids mutually:

$$\frac{k^{25}}{k_0} \text{ for acetic acid} = 5.0\,^{2})$$

propionic ,, $= 5.3$
n. butyric ,, $= 5.2$
isobutyric ,, $= 5.0$,

and differs considerably from that found previously for the cyclic anhydrides. [3])

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[1]) Soc. **97**, 732 (1910), **101**, 1708 (1912) and **103**, 1959 (1913).

[2]) This has been deduced from the above measurements in connexion with those of RIVETT and SIDGWICK (l.c.) and ORTON and JONES. Soc. **101**, 1708 (1912).

[3]) Recueil **31**, 80 (1912).

b. For *iso* and *n* butyric acid the proportion of the hydratation constants = 1 : 1,04, and 1 : 1,07 respectively; that of the dissociation constants 1 : 1,01, and 1 : 1,02 respectively. The branching of a saturated group, appears therefore to exert but little influence on the velocity of hydratation. This is in accordance with the fact that the hydratation constants of the two isomeric *s* dimethylsuccinic anhydrides are proportional to the dissociation constants of the correlated acids. [1])

c. If now we assume provisionally that, other influences being equal, the hydratation constant is proportional to the dissociation constant, the specific influence of the saturated group may then be expressed in figures.

Therefore we have only got to divide the hydratation constants by the dissociation constants; we then obtain, for the influence of this group, for instance at 25°:

		Proportion
For acetic acid	3.92×10^{-3}	
		1.36
For propionic ,,	2.89×10^{-3}	
		1.75
,, n butyric ,,	1.65×10^{-3}	
,, isobutyric ,,	1.58×10^{-3}	

From the corresponding values for butyric acid and isobutyric anhydride follows that the influence of the configuration of the group in regard to other influences must be trifling (see *b*).

The influence of the mass must be, however, very great as the retardation that occurs by the introduction of two methyl groups in the acetic anhydride (= 1.36) is less than that observed by introducing those same groups into the propionic anhydride (= 1.75).

This stronger retarding influence of the ethyl than that of the methyl group also appears from what has been found in the case of the mixed acetic propionic anhydride. The constant thereof lies between the two constants of the acetic and propionic anhydride, but slightly more towards the constant of propionic anhydride.

In the case of the isovaleric anhydride we have met with very great difficulties; the solubility of this substance in water is exceedingly small so that we could not get solutions containing more than 0,005 mol. $^0/_0$.

Owing, however, to the very small velocity with which the hydratation took place and the fairly great conductivity of the isovaleric acid the process could be traced very accurately.

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[1] Rec. **31**, 80 (1912).

Here it appeared that there was no question of a constant; the calculated constant decreased, but so regularly and (after elimination of all possible disturbing influences) so very concordantly, that we were able to conclude that this decrease might be traced to a very definite cause.

The subjoined table shows one of the many measurements.

Isovaleric anhydride at 25°.0.

λ	$\varkappa$	c	$0.4343\, k^{25}$
0	0.0_4670	0.00210	—
1	694	224	0.0247
3	727	244	209
5	757	264	209
7	782	280	201
9	804	294	195
11	822	306	188
14	843	321	179
17	863	335	174
20	879	345	166
25	899	360	156
30	914	371	146
37	929	384	139
45	940	392	123
55	953	401	111
∞	$0.0_3 1027$	463	—

When the constants obtained in the different measurements were plotted against the time, we could draw through the points thus obtained smooth curves which either coincided or ran completely parallel [1]), a sign that not only were we not dealing with experimental errors, but that the fall must be attributed to a disturbing reaction and, looking at the regularity, to a follow-reaction.

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[1]) The latter, because the readings did not always commence exactly at the same moment after the anhydride had been dissolved, as the filtration sometimes took a little longer and because the temperature equilibrium in the resistance vessel was not always attained in the same time.

In consequence of VOERMAN's observations (l. c.) we first believed that the anhydride might be polymerised and that a succession of depolymerisation and hydratation was measured. As, however, the anhydride did not give the least indications of polymerisation even in strongly associating liquids, C_6H_6 and $C_6H_5NO_2$, we gave up this idea in favour of the following assumption.

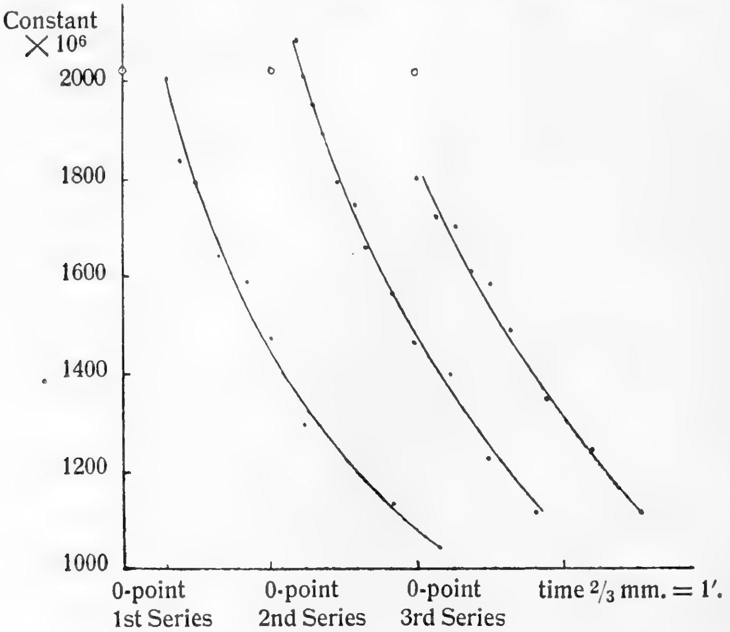
We can imagine the process to be divided into two phases: the first is the union with water or the hydratation proper; the second is the splitting of the hydrate into two molecules of acid.

Now in the case of the lower acid anhydrides the first process will take place very rapidly causing the second one to be measured only; hence, the reaction exhibits the form of the simple unimolecular change.

If the velocity of the first in regard to the second is no longer practically infinite, we are then dealing with the succession of two unimolecular processes occurring in the same direction and the unimolecular-calculated constant will exhibit a regular change [1].

We give here three of these observation series obtained with very carefully purified synthetic *iso*valeric anhydride.

Falling constant of the hydratation of the *iso*valeric anhydride.



The further discussion of these observations in connection with the

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[1] OSTWALD. Lehrbuch Allg. Ch. II, 2, 285.

relation applying to the unimolecular follow reactions will be given elsewhere; we call, however, already now the attention to the fact that Benrath [1]) has found that in glacial acetic acid the reaction between *equivalent* quantities of water and acetic anhydride proceeds unimolecularly, which can only be explained by assuming that in glacial acetic acid they are dissolved jointly as hydrate (in fact that the hydration proceeds exceedingly rapidly) and that this hydrate splits up into the acid molecules [2]).

Further, we have also succeeded in demonstrating the formation of other additional compounds with the acid anhydrides of which those with *iso*valeric anhydride exhibit a greater stability than those with the lower acid anhydrides.

Thus we could isolate the additive products of hydroferricyanic acid with *iso*valeric and heptylic anhydride in a crystalline condition and analyse the same whereas these two gave with 70 % perchloric acid colorations that pointed to additive action.

With great probability we may conclude already now that the conversion of acid anhydrides into acids proceeds in two phases; presumably there first takes place a linking of the anhydride to the watermolecules which occurs very rapidly with the lower terms; this is then succeeded by the splitting reaction which takes place more slowly.

The analogy existing between the acid anhydrides, the esters, and the ethers and between the acid formation, the saponification and the alcohol formation causes the elucidation of the first reaction to become of a more general significance.

If, on further working out the results obtained, it appears that the process studied by us proves with certainty the linking of water followed by hydrolysis, we may expect this to be also the case with the other processes mentioned.

Like in so many other chemical transformations we again get here the impression that the reaction proper is preceded by a previous stage, namely the mutual influence of the molecules.

This is often shown by the formation of an additive product, but here, as in the case of the catalytic phenomena, the reaction proper will proceed more rapidly when this additive product forms more quickly and possesses less stability.

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[1]) Z. Ph. Ch. **67**. 501 (1909).

[2]) Benrath measures the density of a mixture of acetic anhydride, glacial acetic acid and water during the hydration; he finds a change in density of about one unit in the second decimal.

SUMMARY.

1. We determined the progressive change of the acid formation from some aliphatic saturated acid anhydrides in presence of an excess of water at 0° and 25°.
2. In the case of the lower acid anhydrides including the butyric acids this proved to be a unimolecular reaction with a relative small temperature coefficient.
3. As from previous investigations it had appeared that the reaction constant is closely connected with the dissociation constant of the acids forming, it could be deduced, by eliminating this influence, that the hydratation constant decreases as the mass of the saturated group increases, and that the branching of the saturated carbon chain has little influence on this constant.
4. From the fall of the "constant" for the acid formation from *iso*valeric anhydride it was deduced that the formation of acid usually takes place in two phases: *a.* Absorption of water, *b.* splitting of the hydrate; that with the lower acid anhydrides the first reaction occurs very rapidly so that only the last unimolecular reaction gets measured; that in the case of the *iso*valeric anhydride the first reaction no longer takes place infinitely in regard to the second so that we must get the image of a follow-reaction with unequal reaction constants.

Delft, December 1913.

Lab. Org. Chem. Techn. Univ., Delft.

Mathematics. — "*Bilinear congruences and complexes oj plane algebraic curves.*" By Prof. Jan de Vries.

1. We shall consider a doubly infinite system of plane curves of order n, consequently a congruence $[\gamma^n]$. We suppose that through an arbitrary point only *one* curve passes, and that an arbitrary straight line is cut in n points by only *one* curve. The congruence is in that case of the *first order*, and of the *first class*; we shall call it for the sake of brevity a *bilinear congruence*.

As a γ^n of the congruence is determined by a straight line r of its plane φ, all planes φ must pass through a fixed point F, which we shall call the *pole*.

A ray f passing through F (*polar ray*) bears ∞^1 planes φ; the curves γ^n lying in it form a surface Σ of order $(n+1)$, for any point of f lies on only one curve γ^n.

We consider now the surfaces Σ^{n+1}, belonging to the rays f and f'; they have in common the γ^n lying in the plane (ff'), and intersect further along a curve σ of order (n^2+n+1), which passes through F[1].

Through a point S of σ pass two curves γ^n, the planes of which contain successively the straight lines f and f'. S is therefore a *singular point* and lies consequently in ∞^1 curves γ^n. The planes of these γ^n form the pencil with axis FS; the curves themselves lie on a Σ^{n+1}, which has a node in S; for a straight line passing through S meets Σ^{n+1} in $(n-1)$ points situated outside S.

Let f'' be an arbitrary ray through F, $s = FS$ a bisecant of the curve σ; γ^n in the plane $(f''s)$ passes through S. The surface Σ belonging to f'' contains therefore the curve σ and the latter is base-curve of the net which is formed by the ∞^2 surfaces Σ. The γ^n which is determined by an arbitrary point P, forms with σ the base of a pencil belonging to the net.

A γ^n can meet an arbitrary surface Σ^{n+1}, in singular points S only; consequently it rests in $n(n+1)$ points on the *singular curve* σ^{n^2+n+1}, while its plane cuts σ still in the pole F.

A bilinear congruence $[\gamma^n]$ *consists of the curves* γ^n, *which cut a twisted curve of the order* (n^2+n+1) *in* $(n+1)$ *points, and send their planes through a fixed point of that curve*[2].

The curve σ may be represented by

$$\left\| \begin{matrix} a^n_x & b^n_x & c^n_x \\ \alpha_x & \beta_x & \gamma_x \end{matrix} \right\| = 0,$$

hence the $[\Sigma^{n+1}]$ by

$$\begin{vmatrix} \lambda & \mu & \nu \\ a^n_x & b^n_x & c^n_x \\ \alpha_x & \beta_x & \gamma_x \end{vmatrix} = 0,$$

and the congruence $[\gamma^n]$ by the relations

$$\varrho a^n_x + \sigma b^n_x + \tau c^n_x = 0, \qquad \varrho \alpha_x + \sigma \beta_x + \tau \gamma_x = 0.$$

2. The surface Σ formed by the γ^n, which rest in a singular

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[1] σ is of the rank $n(2n^2+n+1)$ and the genus $\frac{1}{2}n(n-1)(2n+1)$; it sends $\frac{1}{2}n^2(n^2+1)$ bisecants through one point.

[2] For $n = 2$ this has been pointed out by MONTESANO ("Su di un sistema lineare di coniche nello spazio", *Atti di Torino*, XXVII, p. 660—690). GODEAUX arrived at the congruence $[\gamma^n]$ by inquiring into *linear* congruences of γ^n of the genus $\frac{1}{2}(n-1)(n-2)$, which possess *one* singular curve, on which the γ^n rest each in $n(n+1)$ points. ("Sulle congruenze lineari di curve piane dotate di una sola curva singolare", *Rend. di Palermo*, XXXIV, p. 288—300).

point S on σ, is cut in $(n+1)$ points by an arbitrary straight line l; consequently σ is an $(n+1)$-fold curve on the surface A of the curves γ^n, which are cut by l. As two surfaces A apart from σ can only have in common a number of γ^n, which agrees with the order of A, we have for the determination of that order x the relation

$$x^2 = nx + (n+1)^2 (n^2+n+1);$$

from which ensues $x = (n+1)^2$.

The γ^n *resting on a straight line* l *form a surface of order* $(n+1)^2$ *on which the* γ^n, *of which the plane passes through* l, *is an* n*-fold curve; the singular curve is* $(n+1)$*-fold.*

A is cut $n(n+1)^2$ times by an arbitrary γ^n of the congruence; from this appears again that γ^n rests in $n(n+1)$ points on σ.

Two arbitrary straight lines are cut by $(n+1)^2$ *curves of the congruence.*

A plane φ passing through l intersects A moreover along a curve, which is apparently cut $n(n-1)$ times on l by the γ^n, of which the plane passes through l; in each of the remaining $(n+1)^2-1-n(n-1) = 3n$ points φ is touched by a γ^n.

The curves γ^n, *which touch a given plane have their points of contact on a curve of order* $3n$, *which possesses* (n^2+n+1) *double points.*

The last mentioned observation ensues from the fact that the surface Σ^{n+1}, which has a node in a singular point S, is cut by φ along a curve with node S; φ is therefore touched in S by two γ^n.

The curve φ^{3n} found just now is the locus of the coincidences of the involution formed from collinear sets of n points in which φ is cut by $[\gamma^n]$.

3. The surface A belonging to an arbitrary straight line, not lying in φ, has apart from the (n^2+n+1) points S $3n(n+1)^2 - 2(n+1)(n^2+n+1) = (n+1)(n^2+n-2) = (n+2)(n^2-1)$ points in common with φ^{3n}.

There are $(n+2)(n^2-1)$ *curves in* $[\gamma^n]$, *which touch a given plane, and at the same time cut a given straight line.*

We can arrive at the last mentioned result in an other way yet.

The surface Σ^{n+1}, which contains the γ^n, the planes of which pass through a polar ray f, is cut by a straight line l in $(n+1)$ points; so the planes of $(n+1)$ curves γ^n pass through f, which curves rest on l. Consequently the planes of the γ^n lying on A envelop a *cone of class* $(n+1)$.

A plane φ cuts Σ^{n+1} along a curve φ^{n+1}, which passes through the point of intersection of f, and sends $(n+1)n-2 = (n+2)(n-1)$

tangents through that point. From this follows that the planes of the γ^n, touching φ, envelop a *cone of class* $(n+2)(n-1)$.

Each common tangent plane of the two cones, contains a γ^n, which cuts l and touches φ; for the number of those curves we find therefore again $(n+2)(n^2-1)$.

The two cones of class $(n+2)(n-1)$, which are enveloped by the planes of the γ^n, which touch two given planes have $(n+2)^2(n-1)$ tangent planes in common. *As many curves* γ^n *consequently touch two given planes.*

4. A surface Σ^{n+1}, belonging to the polar ray f, contains a number of γ^n with a node; such a γ^n is the intersection of Σ with a tangent plane passing through f.

In order to determine the number of those planes, we consider the points which Σ outside f, has in common with the polar surfaces α^n and β^n of two points A and B lying on f. A plane φ passing through f cuts these surfaces along two curves a^{n-1} and b^{n-1}, which cut f in two groups of $(n-1)$ points A_k and B_k. If φ is made to revolve round f, these sets of $(n-1)$ points describe two projective involutions so that a correspondence $(n-1, n-1)$ arises on f. In each coincidence C, f is cut by two curves a^{n-1}, b^{n-1} lying in the same plane φ; there α^n and β^n have therefore the same tangent plane which contains at the same time the tangent of the curve φ of the order (n^2-1), which α^n and β^n have in common, apart from f.

The $2(n-1)$ points C are at the same time the coincidences of the involution of the n^{th} degree, which is determined on f by the curve γ^n, out of which Σ is built up; in each point C, Σ is therefore touched by the plane φ and moreover by the curve φ. Consequently ϱ has on f $4(n-1)$ points in common with Σ; the number of intersecting points of φ and Σ lying outside f amounts therefore to $(n^2-1)(n+1) - 4(n=1) = (n-1)^2(n+3)$.[1]

Through each polar ray f pass consequently the planes of $(n-1)^2(n+3)$ nodal curves γ^n_δ.

The planes of the nodal curves γ^n_δ envelop a *cone of class* $(n-1)^2(n+3)$; the planes of the γ^n, which rest on a straight line l, envelop a cone of class $(n+1)$. *From this follows that the nodal curves* γ^n_δ *form a surface* Δ *of order* $(n+3)(n+1)(n-1)^2$.

On a straight line f lie $n(n-1)^2(n+3)$ points of the nodal curves γ^n_δ, of which the planes pass through f; in the pole F the surface Δ is cut by f in $(n+3)(n-1)^2$ points.

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[1] For $n+1=3$, we duly find the five pairs of lines which rest on a straight line of a cubic surface.

Let S be a point of the singular curve σ; the ray FS is cut in S by the $(n+3)(n-1)^2$ curves $\gamma_\delta{}^n$, of which the planes pass through FS.

In connection with what was mentioned above we may therefore conclude that the singular curve σ is $(n+3)(n-1)^2$-fold on the surface Δ.

5. If all γ^n pass through the pole F, so that the latter is a *fundamental point* of the congruence, then all surfaces Σ^{n+1} have a node in F. Two surfaces have four points in F in common in that case; one of them belongs to the γ^n, which forms part of the intersection, consequently the *singular curve* σ has now a *triple point* in F. In an arbitrary plane φ passing through F the two Σ have $(n+1)^2-4$ points in common, apart from F, $(n-1)$ of those points lie on the common γ^n, the remaining (n^2+n-2) on σ.

In those points σ is cut by the curve of the congruence lying in φ. The curves γ^n consequently pass through the triple point of the singular curve, and rest moreover in $(n+2)(n-1)$ other points on it.

Any plane passing through a tangent t_k in F to σ contains a γ^n, which touches t_k in F. In the plane passing through two of those tangents lies therefore a $\gamma_\delta{}^n$, which has a node in F. Each of the three bitangent planes of σ which are determined by the three tangents in F contains therefore a $\gamma_\delta{}^n$ with node F.

The quadric cones of contact in F of the surfaces of the net $[\Sigma^{n+1}]$ form apparently a net which has as base edges the three tangents of the singular curve σ. To that net belongs the figure consisting of the plane $t_k\,t_l$ with an arbitrary plane passing through t_m; so the net $[\Sigma^{n+1}]$ contains three systems of surfaces, which have a biplanar point in F; the edge of the pair of planes into which the cone of contact degenerates lies in one of the three planes $t_k\,t_l$.

6. We shall now consider a triply infinite system of plane algebraic curves γ^n, which form a *bilinear complex* $\{\gamma^n\}$[1]. In an arbitrary plane lies therefore *one* γ^n, and the curves γ^n, which pass through a point P, lie in the planes of a *pencil* (cone of the first class); the axis p of that pencil we shall call for the sake of brevity, the *axis of* P.

The curves of $\{\gamma^n\}$, of which the planes pass through an arbitrary straight line r form apparently a surface of order $(n+1)$, which we

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[1] The bilinear complexes of conics have been fully treated by D. MONTESANO ("I complessi bilineari di coniche nello spazio", *Atti R. Acc. Napoli*, XV, ser. 2*a*, n^0. 8).

shall indicate by Σ_r^{n+1}. Through a point P of r passes only one γ^n, namely the curve lying in the plane (pr).

The surface Σ_p^{n+1} belonging to an axis p has a node in P; for a line l passing through P cuts the γ^n of the plane (pl) in $(n-1)$ points lying outside P.

If r is made to revolve in a plane φ around a point O then Σ_r^{n+1} describes a *pencil.* In order to determine the surface Σ which passes through an arbitrary point P, we have only to find the ray r, which cuts the axis p of P. The base of this pencil consists of the curve γ^n lying in φ and a twisted curve φ^{n^2+n+1}, which cuts γ^n in $n(n+1)$ points.

Any point P of this curve lies on ∞^1 curves γ^n; its axes p must meet all the rays of the pencil (O, φ), consequently pass through O.

To the net of rays of the straight lines r, lying in φ, corresponds a *net* of surfaces Σ_r^{n+1}. Through two arbitrary points P, P' passes the surface belonging to the straight line r, which cuts the axis p, p'.

7. Let us now consider the surfaces of this net belonging to three straight lines, r, r', r'' of φ, which do not pass through one point. The curve ϱ^{n^2+n+1}, which two of these surfaces have in common, cuts the third surface in $(n+1)(n^2+n+1)$ points. To these points belong $n(n+1)$ points of the γ^n lying in φ.

Let H be one of the remaining $(n+1)(n^2+n+1) - (n+1)n = (n+1)(n^2+1)$ intersections. Through H pass the curves γ^n lying in the three planes which connect H with $r, r', r'_{,}$; these planes do not belong to a pencil, consequently H bears ∞^2 curves γ^n and is therefore a *cardinal point* (fundamental point) of the complex $\{\gamma^n\}$. Any straight line through H is apparently an axis and determines by means of its intersection with φ, a pencil (Σ^{n+1}), consequently a curve ϱ^{n^2+n+1}.

The complex $\{\gamma^n\}$ *has* $(n+1)(n^2+1)$ *cardinal points; they are at the same time cardinal points of the complex of rays* $\{p\}$ *and of the complex of curves* $\{\varrho^{n^2+n+1}\}$.

The cardinal points are apparently base points of the net $\{\Sigma^{n+1}\}$ belonging to the plane φ, or, more exactly expressed, of all the nets which are indicated by the planes φ in space.

8. Let us now consider the curves of $\{\gamma^n\}$ which send their planes through an arbitrary point F. Through a point P passes the γ^n of the plane (Fp); through a straight line r passes the plane (Fr) and this plane contains *one* γ^n. So we have set apart out of the complex a *bilinear congruence* $[\gamma^n]$ which has F as *pole.* Its polar rays are the axes p of the points P of the singular curve σ^{n^2+n+1}; they project this curve out of the pole F lying on it, consequently form a cone of order $n(n+1)$. From this follows that *the axes of* $\{\gamma^n\}$ *form a complex of rays of order* $n(n+1)$.

In any plane passing through a cardinal point H lies a γ^n, which passes through H. The ∞^2 γ^n passing through H form therefore a special congruence $[\gamma^n]$, which has H as fundamental point; the singular curve σ of this congruence has therefore a triple point in H (§ 5); it is the σ^k, which has H_k as pole.

Each point H *is triple point of a singular curve* σ, *which passes through the remaining cardinal points.*

This curve is base curve of a net of surfaces Σ, which have all a node in H.

The planes of the nodal curves $\gamma^n{}_\delta$ envelop a surface of class $(n-1)^2(n+3)$, for this is the number of tangent planes of $\Sigma_r{}^{n+1}$, which pass through a straight line r (§ 4).

The curves $\gamma^n{}_\delta$ form apparently a *congruence* of which the *order* and *class* are $(n-1)^2(n+3)$.

9. We now assume a tetrahedron of coordinates and consider the net of surfaces Σ belonging to the straight lines of the plane $x_4 = 0$. This net may then be represented by

$$\alpha \begin{vmatrix} a^n{}_x & d^n{}_x \\ x_1 & x_4 \end{vmatrix} + \beta \begin{vmatrix} b^n{}_x & d^n{}_x \\ x_2 & x_4 \end{vmatrix} + \gamma \begin{vmatrix} c^n{}_x & d^n{}_x \\ x_3 & x_4 \end{vmatrix} = 0.$$

The cardinal points are therefore found from

$$\left\| \begin{matrix} a^n{}_x & b^n{}_x & c^n{}_x & d^n{}_x \\ x_1 & x_2 & x_3 & x_4 \end{matrix} \right\| = 0.$$

From this ensues readily that the curves of the complex may be represented by the relations:

$$\alpha a^n{}_x + \beta b^n{}_x + \gamma c^n{}_x + \delta d^n{}_x = 0 \;,\; \alpha x_1 + \beta x_2 + \gamma x_3 + \delta x_4 = 0.$$

If we consider here α, β, γ as given, but δ as variable, then there arises by elimination of δ the above mentioned equation of the surface Σ belonging to the straight line $x_4 = 0$, $\alpha x_1 + \beta x_2 + \gamma x_3 = 0$.

For the curves passing through a point Y is

$$\Sigma\, \alpha a^n_y \equiv \alpha a^n_y + \beta b^n_y + \gamma c^n_y + \delta d^n_y = 0 \quad \text{and} \quad \Sigma\, \alpha y_1 = 0.$$

By elimination of $\alpha, \beta, \gamma, \delta$ out of these equations and $\Sigma\, \alpha a^n_x = 0$, $\Sigma\, \alpha x_1 = 0$, we find for the surface Σ^{n+1} belonging to Y, the equation

$$\left| \, y_1 \quad a^n_y \quad x_1 \quad a^n_x \, \right| = 0.$$

The *axis* of Y is indicated by

$$\left\| \, y_1 \quad a^n_y \quad x_1 \, \right\| = 0.$$

In order to determine the surface Σ^{n+1} belonging to the straight line which joins the points Y and Z, one has to eliminate $\alpha, \beta, \gamma, \delta$ out of $\Sigma\, a y_1 = 0$, $\Sigma\, a z_1 = 0$, $\Sigma\, a x_1 = 0$ and $\Sigma\, a a^n_x = 0$; then one finds

$$\left| \begin{matrix} y_1 & z_1 & x_1 & a^n_x \end{matrix} \right| = 0,$$

while the straight line YZ is indicated by

$$\left\| \begin{matrix} y_k & z_k & x_k \end{matrix} \right\| = 0.$$

Through the point X pass the axes of the points Y, for which we have

$$\left| \begin{matrix} y_1 & a^n_y & x_1 \\ y_2 & b^n_y & x_2 \\ y_3 & c^n_y & x_3 \end{matrix} \right| = 0 \quad \text{and} \quad \left| \begin{matrix} y_2 & b^n_y & x_2 \\ y_3 & c^n_y & x_3 \\ y_4 & d^n_y & x_4 \end{matrix} \right| = 0.$$

These surfaces of order $(n+1)$ have the curve

$$\left\| \begin{matrix} y_2 & b^n_y & x_2 \\ y_3 & c^n_y & x_3 \end{matrix} \right\| = 0$$

in common, which is of order n, but is not situated on the two other surfaces of order $(n+1)$, which are indicated by

$$\left\| \begin{matrix} y_1 & a^n_y & x_1 \end{matrix} \right\| = 0$$

The last mentioned relations determine therefore a curve of order $(n^2 + n + 1)$ as locus of the points Y. From this ensues again that the axes form a complex of rays of order $n\,(n+1)$.

Mathematics. — "*A bilinear congruence of twisted quartics of the first species.*" By Prof. JAN DE VRIES.

1. As we know, we distinguish with congruences of algebraic twisted curves two characteristic numbers, called *order* and *class*.

The *order* indicates how many curves pass through an arbitrary point, the *class* the number of curves which have an arbitrarily chosen straight line as a bisecant. If both numbers are one the congruence is called *bilinear*. In volume XVI of the *Rend. del Circ. mat. di Palermo* (p. 210) E. VENERONI has proved that there exist principally two kinds of bilinear congruences of twisted cubics. An analogous inquiry concerning congruences of twisted quartics of the first species, ϱ^4, has not been made till now. [1])

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[1]) The bilinear congruences of conics have been treated by MONTESANO (Atti di Torino XXVII p. 660).

In a communication which appeared in Volume XIV of these *Proceedings,* I have (p. 255) considered the bilinear congruence $[\varrho^4]$, which arises if the quadrics of two pencils are made to intersect.[1]

It is not difficult to understand that no bilinear congruences of curves of a higher order can be produced by two pencils of surfaces. For, if these pencils are of the degrees m and n, they intersect an arbitrary line in two involutions of the degrees m and n and these have in common $k=(m-1)(n-1)$ pairs; so we find a congruence $[\varrho^{mn}]$ of the first order, and the class $(m-1)(n-1)$; only for $m=n=2$ we find $k=1$.

2. In order to arrive at another group of bilinear congruences, I consider a net of cubic surfaces $[\Phi^3]$. Through an arbitrary point P pass ∞^1 surfaces Φ^3, which form a pencil included in the net, of which pencil the base curve in the general case will be a twisted curve ϱ^9 of genus 10. All the curves ϱ^9 included in the net consequently form a congruence of order *one.* On an arbitrary line the net determines a cubic involution of the second rank; the latter possesses as we know a neutral pair N_1, N_2; all the ϱ^9 through N_1 pass through N_2 as well, consequently the congruence is also of the first *class,* therefore *bilinear.*

If all the Φ^3 have a curve in common, the curves ϱ^9 degenerate into an invariable and a variable part, and a bilinear congruence of curves of a lower order is found. We shall now consider the case in which we have to do with a congruence $[\varrho^4]$.

3. Let ϱ^5 be a twisted curve of order five, and let the genus be 2, so the remaining section of a Φ^3 and a Φ^2, which have a straight line in common. Any surface Φ^3 passing through 14 points of ϱ^5 contains this curve[2]); consequently the Φ^3 passing through ϱ^5 and three arbitrarily chosen points H_1, H_2, H_3, form a net. Two of these surfaces have besides ϱ^5, a ϱ^4 of the 1st species in common, which intersects ϱ^5 in *eight* points[3]). With a third Φ^3, ϱ^4 has 12 points in common, of which 8 lie on ϱ^5, the other four, and to them belong of course H_1, H_2 and H_3 lie apparently on all Φ^3, therefore on all ϱ^4.

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[1]) If the bases of the two pencils have a straight line in common, one of the two congruences $[\varrho^3]$ found by VENERONI arises.

[2]) R. STURM, *Synthetische Untersuchungen über Flächen dritter Ordnung* (1867, p. 234). P. H. SCHOUTE, *La courbe d'intersection de deux surfaces cubiques et ses dégénerations* (Archives Teyler 1901, t. VII, p. 219). M. STUYVAERT, *Cinq études de géométrie analytique* (Mem. Soc. Liége, 1907, t. VII, p. 40).

[3]) SCHOUTE, (l. c. p. 241), STUYVAERT, (l. c. p. 41).

Here we have consequently *a bilinear congruence* $[\varrho^4]$ with *four cardinal points* H_k and a *singular curve* ϱ^5; i.e. all ϱ^4 pass through the four cardinal points and rest in 8 points on ϱ^5 [1]).

4. Let t be a trisecant of ϱ^5; the pencil of net surfaces determined by a point of t has for base the complex of ϱ^5, t and a plane cubic γ^3, which has a point T with t in common, and 5 points with ϱ^5. This γ^3 must contain the four cardinal points H; *consequently the cardinal points are situated in a plane* φ.

Any curve γ^3 connects the 4 cardinal points and the 5 points R_k, in which ϱ^5 cuts the plane φ, with the intersecting point T of the trisecant belonging to it. As the trisecants form the quadratic ruled surface Φ^2, on which ϱ^5 lies, the points R, together with T may be connected by a conic τ^2.

The curves γ^3 form a pencil with base (R_k, H_k); any γ^3 intersects τ^2 in the point T, through which the straight line t passes, which, considered together with γ^3 belongs to the congruence $[\varrho^4]$ [2]).

The locus of the degenerate figures $(\gamma^3 + t)$ is apparently the complex of Φ^2 and φ, and consequently belongs to the net $[\Phi^3]$.

5. Let b be one of the four bisecants of ϱ^5, which pass through the cardinal point H_k. All the Φ^3 which contain b, have moreover a ϱ^3 in common, which has b as bisecant and rests in 6 points on ϱ^5.

Consequently there are *sixteen figures* $(\varrho^3 + b)$ in $[\varrho^4]$.

A third group of complex figures is formed by pairs of conics (α^2, β^2). Let α^2 be a conic passing through H_1, H_2, intersecting ϱ^5 in 4 points, the Φ^3 passing through α^2 and ϱ^5 have an other conic β^2 in common, which intersects α^2 in 2 points, ϱ^5 in 4 points and passes through H_3, H_4

The number of α^2 we deduce using the law of permanency of the number. We replace ϱ^5 by the complex of a σ^3 and a σ^2, which have three points in common; through a point P pass consequently 3 straight lines, which rest on σ^3 and σ^2; with the bisecant of σ^3 they form the 4 straight lines which replace the 4 bisecants of ϱ^5; consequently $(\sigma^3 + \sigma^2)$ is to be considered as a degeneration of ϱ^5. In any plane passing through H_1 and H_2 lies a conic φ^2 connecting these points with 3 points of σ^3; as the straight line H_1H_2 cannot

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[1]) If the base of the net consists of a curve ϱ^6, of genus 3, and a cardinal point H, the second bilinear congruence $[\varrho^3]$ is formed.

[2]) That the figure $(\gamma^3 + t)$ is a special case of a ϱ^4, appears from the fact that through an arbitrarily chosen point P, two straight lines may be drawn which intersect γ^3 and t; they replace the bisecants which ϱ^4 sends out through P.

apparently be a part of a degenerate φ^2, the φ^2 form a quadric. This is cut by σ^2 in 4 points; among them are the 3 common points of σ^3 and σ^2; through the fourth intersecting point passes a φ^2, which has four points in common with the figure $(\sigma^3 + \sigma^2)$.

From this we conclude that *one* conic α^2 can be drawn through H_1 and H_2. As each α^2 is coupled with a β^2 (which passes in that case through H_3 and H_4), $[\varrho^4]$ contains *three figures* $(\alpha^2 + \beta^2)$.

6. Through a point S of the singular curve ϱ^5 pass ∞^1 curves ϱ^4. They cut the plane φ in the points H. To this system of ϱ^4 belongs, however, also the figure consisting of the trisecant t passing through S and a γ^3 lying in φ. From this ensues that the locus of the ϱ^4 meeting in S, is a cubic surface Σ^3, passing through ϱ^5 and the points H, and consequently belongs to the net $[\Phi^3]$.

An arbitrary line passing through S, is a bisecant of *one* ϱ^4, and so intersects Σ^3, apart from S in *one* point. Consequently Σ^3 has a double point in S. Through S pass 6 straight lines of Σ^3, one of them is of course the t mentioned before; each of the remaining 5 is a bisecant p of ∞^1 curves ϱ^4, so a *singular bisecant*.

All the ϱ^4 intersecting p twice pass through S; so they determine on p a parabolic involution, of which all pairs have the point S in common; we shall call p a *singular bisecant of the first species.*

Through each point of ϱ^5 pass therefore five singular bisecants of the first species.

Any line h passing through a cardinal point H is as well a singular bisecant of the first species.

The monoids Σ^3 having two points of ϱ^5 as double points, intersect apart from ϱ^5 in a ϱ^4. Through any two points S passes therefore only *one* curve of the congruence.

7. Let q be a bisecant of a ϱ^5, and at the same time a secant of ϱ^4. The surface Φ^3 passing through ϱ^5 and ϱ^4 and a point of q contains q, and belongs to the net $[\Phi^3]$. Consequently all Φ^3 passing through a point Q of q will cut this straight line moreover in a second point Q'. Consequently q is a bisecant of ∞^1 curves ϱ^4, and the pairs of the intersections Q,Q' form an involution. We call q a *singular bisecant of the second species.*

In order to find the number of lines q that pass through a point P, we consider the cubic cone k^3, which out of P projects the ϱ^4 containing P, and the cone k^5 which has P as vertex and ϱ^5 as curve of direction. To the 15 common generatrices belong the lines drawn to the eight intersecting points of ϱ^4 and ϱ^5. The remaining

7 are bisecants of ϱ^4 intersecting ϱ^5, therefore lines q. Consequently the lines q form a *congruence of order seven.*

We can also arrive at this result in another way. A straight line passing through P is generally speaking, a bisecant of *one* ϱ^4; we call R, R' its intersections with ϱ^4 and consider the surface π, which is the locus of the pairs R, R'. On any generatrix of the cone k^3 one of those points lies in P, hence π has in P a triple point with k^3 as tangent cone; π is consequently a surface of order 5. It passes through ϱ^5, and has nodes in the four cardinal points. For an arbitrary ϱ^4 has in common with π the intersections with the bisecants which it sends through P, and in 8 points of ϱ^5, so twice in each point H.

Now π^5 and k^3 have in common the ϱ^4 which passes through P; further they can, by reason of the definition of π, only have lines in common which contain ∞^1 pairs R, R' each. Therefore *eleven singular bisecants* pass through P. To these the four straight lines $h_k = PH_k$ belong; for through any point of PH_k passes a ϱ^4, which meets this straight line again in the cardinal point H_k, so that PH_k is a singular straight line of the first species (which, however, does not rest on ϱ^5, and consequently may not be interchanged with a straight line p). The remaining 7 singular bisecants passing through P are therefore straight lines q.

For a point S of ϱ^5 the surface π^5 degenerates, and consists of the monoid Φ^3 with node S and a quadratic cone, formed by the straight lines q, which intersect ϱ^5 in S.

In an arbitrary plane lie five points of ϱ^5, consequently 10 straight lines q; they belong therefore to a *congruence of rays of class ten.*

The singular bisecants of the second species form a congruence (7, 10), *which has* ϱ^5 *as a singular curve.*

The section of π^5 with a plane passing through P is a curve with a triple point, consequently of class 14, of its tangents 8 pass through P. Therefore the tangents of the curves ϱ^4 form a *complex of order eight.*

8. The ϱ^4 which intersect a given line l, form a surface Λ, of which we intend to determine the order $\varkappa$. Any monoid Φ^3 contains three ϱ^4, which intersect l, and rest in the vertex S on ϱ^5; consequently ϱ^5 is a triple curve of Λ.

The surfaces Λ, Λ' belonging to two lines l, l' have, besides the threefold curve ϱ^5 only the $\varkappa$ curves ϱ^4 in common, resting on l and l'. So we have the relation $\varkappa^2 = 4\varkappa + 3^2.5$, hence $\varkappa = 9$.

On Λ^9 lies one trisecant t; for the curve γ^3, which intersects l, determines on τ^2 the point T of the trisecant with which it forms a degenerate ϱ^4 (§ 4).

The curve $\varrho^4{}_l$, which has l as a bisecant belongs to two points of l, and is consequently a twofold curve of Λ^9.

The locus of the ϱ^4 intersected by l is therefore a *surface of order nine* with a *twofold curve* $\varrho^4{}_l$, a *triple curve* ϱ^5 and two straight lines l and t.

9. A plane through l intersects Λ^9 in a curve λ^8; the latter has the two intersections of $\varrho^4{}_l$ and six points R in common with l; in each point R, λ is touched by a ϱ^4.

The points in which a plane is touched by curves ϱ^4 lie therefore on a curve γ^6; it is the *curve of coincidences* of the *quadruple involution* Q^4, in which the plane λ is intersected by the congruences $[\varrho^4]$.

The five intersections S_k of ϱ^5 with λ are apparently *singular points* of Q^4; to S_k are namely conjugated ∞^1 triplets of points, lying on the cubic curve $\sigma^3{}_k$, with double point S_k, in which the monoid Φ^3 (with vertex S_k) is intersected by λ. In S_k λ is therefore touched by two ϱ^4; the *curve of coincidences* γ^6 has consequently nodes in each of the five points S_k, and in S_k the same tangents as $\sigma_k{}^3$.

Any point D of the conic δ^2 through S_k is the intersection of a trisecant t, consequently determines a quadruple, of which the remaining three points are produced by the intersection of the curve γ^3 coupled with t. On the section f of φ we have therefore a cubic involution F^3, of which the groups are completed into quadruples of Q^4 by the points D. It is evident that Q^4, as long as λ remains an arbitrary plane, cannot possess any other collinear triplets.

In each of the points of intersection T_1, T_2 of f with τ^2 (§ 4) a t is cut by a γ^3, consequently these points are coincidences of the Q^4. The remaining coincidences, lying on f, belong to the involution F^3, from this appears again that the order of the curve of coincidences is *six*.

As the singular point S_1 lies on δ^2 and therefore may be considered as a point D, the curve $\sigma_1{}^3$ is intersected by f in a triplet of the cubic involution $I_1{}^3$, of which the groups are completed into quadruples of Q^4 by S_1. As $I_1{}^3$ cannot possess a second collinear triplet, it is not a central involution; so it can be determined in ∞^1 ways by a pencil of conics of which the base points are S_1, an arbitrary point of $\sigma_1{}^3$, and moreover two points of the line f.

10. Any coincidence of the Q^4 is completed into a quadruple by two *complementary* points. The locus δ of those points which we shall call the *complementary curve* has apparently *quadruple points* in S_k; for I_k^3 has four coincidences. Of the four coincidences of F^3, four of the complementary points lie on δ^2; with this conic the curve δ has therefore $4 + 5 \times 4 = 24$ points in common. Consequently the *complementary curve* is of order 12.

The curves ϱ^4, which touch the plane λ in the points of the curve of coincidences γ^6, intersect λ moreover on the complementary curve δ^{12}; so they form a surface of order 24, which passes eight times through the curve ϱ^5.

This surface is intersected by a plane λ' along a curve of order 24 with 5 octuple points S_k. As the curve of coincidences γ'^6 lying in λ' has double points in S_k the two curves outside S_k have $24 \times 6 - 5 \times 8 \times 2 = 64$ points in common. Consequently there are 64 curves ϱ^4, *touching two given planes.*

The surface Δ^9 belonging to the straight line l intersects an arbitrary plane φ along a curve φ^9, which has 5 triple points on ϱ^5. As the curve of coincidences φ^6 lying in φ has 5 nodes on ϱ^5, it intersects φ^9 moreover in $9 \times 6 - 5 \times 3 \times 2 = 24$ points. From this appears once more that the curves ϱ^4, which touch a given plane, form a *surface of order* 24. At the same time, the fact that the complementary curve is of order 12, is confirmed.

Chemistry. — "*Equilibria in ternary systems*". XII. By Prof. Schreinemakers.

We have seen in the previous communication that the saturation-curve under its own vapour-pressure of the temperature T_H (the point of maximumtemperature of the binary system $F + L + G$) is either a point [fig. 5 (XI)] or a curve [fig. 6 (XI)]. We shall now examine this case more in detail.

If we calculate $\frac{dy}{dx}$ for this curve in the point H from (6) and (7) (XI), then we find an infinitely great value. The curve going through H in fig. 6 (XI) and the curve disappearing in H of figure 5 (XI) come in contact, therefore, in H with the side BC. Now we take a temperature somewhat lower than T_H. The saturationcurve under its own vapour-pressure terminates then in two points n and h situated on different sides of and very close to H. [n and h in fig. 4—6 (XI) may be imagined very close to H.] As the saturationcurve under its own vapour-pressure touches BC in H, the tangent in n and the tangent in h to the curve, going through these points, will yet be almost parallel BC.

Because the equilibria $F +$ liquid $n +$ vapour n_1 and $F +$ liquid $h +$ vapour h_1 differ but very little from one another, the perspective concentrations S and S_1 (see the previous communication) will be, on addition of a third substance, also approximately equal. Therefore, when in the one equilibrium $S > S_1$, this is also the case in the other. Of course the same applies to $S < S_1$. Now we distinguish, according as the substance expands or contracts on melting, two principal cases.

1. F expands on melting ($V > v$). The point H is then situated with respect to F as in fig. 4—6 (XI) viz. between F and C, but close to F; ΔV is negative between F and H, positive in the other points of BC. From the situation of n and h with respect to F, it follows that S and S_1 are both positive. We distinguish $S > S_1$ and $S < S_1$.

a. $S > S_1$. As ΔV is positive in h and negative in n, it follows from our previous communication that the pressure decreases from h along the saturationcurve under its own vapour-pressure and it increases from n. In which direction shall this curve now proceed from h? As the tangent in h coincides almost with BC, the curve must go from h either almost in the direction towards n or almost in opposite direction. We find the first in fig. 5, the second in fig. 6 (XI). In order to determine this direction, it is to be considered that the region $L—G$ shifts on decrease of pressure from h towards n, so that the pressure decreases in this direction. As the pressure along the saturationcurve under its own vapour-pressure must also decrease from h, this curve must therefore, also go from h almost in the direction towards n. It has, therefore, from h a direction as in fig. 5 (XI). As the tangent in n coincides almost with BC, the curve must go from n either almost in the direction towards h or almost in opposite direction. Considering that the region $L—G$ shifts on increase of pressure from n towards h, so that the pressure increases from n towards h and further that the pressure along the saturationcurve under its own vapour-pressure must also increase from n, we see that this curve must go, therefore, also from n almost in the direction towards h.

The saturationcurve under its own vapour-pressure has, therefore, a form as curve hn in fig. 5 (XI); it is situated, therefore, close to the side BC and it disappears at T_H in the point H.

b. $S < S_1$. In a similar way as above we find that the pressure along the saturationcurve under its own vapour-pressure increases from h and decreases from n. Further we find that this curve must have in the vicinity of n and h a direction as in fig. 6 (XI). As further the pressure in h is greater than in n, therefore on this curve as well a point of maximum- as a point of minimumpressure must be situated. Consequently, we obtain a curve hn, as in fig. 6 (XI), this does not disappear at the temperature T_H, but it forms a curve, touching the side BC in H.

2. F melts with decrease of volume ($V < v$). Now the points H and H_1 are no more situated, as in the previous case, between F and C. From the binary equilibrium $F + L + G$ it follows that H is situated between F and B; the point H_1 may be imagined as well between F and C as between F and B. In the last case H_1 should be situated between F and H and therefore very close to H; the region L—G should then be very narrow in the vicinity of the side BC, which is only possible in very exceptional cases. Therefore we consider only the first case: H is situated between F and B, and H_1 between F and C.

If we take two points n and h close to H and the corresponding points n_1 and h_1 close to H_1 then we see that S and S_1 have an opposite sign. If further we keep in mind that ΔV is negative between F and H and positive in the other points of BC, then it follows, in a similar way as above, that curve nh must have a form as in fig. 5 (XI). Therefore, it disappears at T_H in the point H. Consequently, we obtain a diagram as in fig. 5 (XI), but with this difference, that H is situated now between F and B.

Contemplating the boilingpointcurves of F, we obtain diagrams as fig. 5 and 6 (XI), the arrows must then however, indicate in opposite direction. Further we must imagine the point of maximum temperature H to be replaced by the point of maximum pressure Q of the binary equilibrium $F + L + G$. ΔW is negative between F and Q, positive in the other points of BC. From the position of Q and Q_1 with respect to F, it follows that S and S_1 are both positive. We distinguish two cases.

a. $S > S_1$. We find that the boilingpointcurve hn has a form as in fig. 5 (XI); the arrows must, however, indicate in opposite direction. Therefore, this curve disappears under the pressure P_Q in the point Q.

b. $S < S_1$. The boilingpointcurve hn has a form as in fig. 6 (XI); the arrows must, however, indicate in opposite direction. Therefore the curve does not disappear in Q under the pressure P_Q.

If we sum together the results obtained above, we have :

1. F melts with increase of volume. The saturationcurve under its own vapour-pressure disappears, when is raised the temperature in H [fig. 4 (XI)] when the concentration of the new substance is greater in the liquid than in the vapour. It does not disappear in H [fig. 6 (XI)] when the concentration of the new substance is smaller in the liquid than in the vapour.

2. F melts with decrease of volume. The saturationcurve under its own vapour-pressure disappears, when is raised the temperature in H [Fig. 5 (XI), wherein however H must be situated between F and B]

3. The boilingpointcurve disappears, on increase of P in Q [fig. 5 (XI)], when the concentration of the new substance is greater in the liquid than in the vapour. It does not disappear in Q [fig. 6 (XI)] when the concentration of the new substance is smaller in the liquid than in the vapour. We mean of course, with "concentration" above "perspective concentration".

Now we will deduce in another way the relations in the vicinity of the point H or Q. The saturationcurve under its own vapour-pressure is fixed by the equations (1) (II), when we put therein $a=0$ and when we keep T constant. As $\frac{\partial Z}{\partial x}, \frac{\partial^2 Z}{\partial x^2}$, etc. become infinitely great for $x=0$, we shall put

$$Z = U + RTx \log x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

so that all differential quotients of U with respect to x, remain finite. We put in the same way:

$$Z_1 = U_1 + RTx_1 \log x_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

so that the same applies to U_1. Then we have:

$$\frac{\partial Z}{\partial x} = \frac{\partial U}{\partial x} + RT(1 + \log x) \quad ; \quad \frac{\partial Z}{\partial y} = \frac{\partial U}{\partial y} \quad ; \quad \frac{\partial Z}{\partial P} = \frac{\partial U}{\partial P} = V \; . \quad (3)$$

and similar relations for Z_1 and U_1.

The equations 1 (II) then become:

$$x\frac{\partial U}{\partial x} + (y-\beta)\frac{\partial U}{\partial y} + RTx - U + \zeta = 0 \quad . \quad . \quad . \quad . \quad (4)$$

$$x_1\frac{\partial U_1}{\partial x_1} + (y_1-\beta)\frac{\partial U_1}{\partial y_1} + RTx_1 - U_1 + \zeta = 0 \, . \quad . \quad . \quad . \quad (5)$$

$$\frac{\partial U}{\partial x} + RT(1 + \log x) = \frac{\partial U_1}{\partial x_1} + RT(1 + \log x_1) \quad . \quad . \quad . \quad (6)$$

$$\frac{\partial U}{\partial y} = \frac{\partial U_1}{\partial y_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In the points H and H_1 of figs. 4—6 (XI), the pressure is equal to P_H, $x=0$ and $x_1=0$; further we put $y=(y)_0$ and $y_1=(y_1)_0$. For a point in the vicinity of BC on this saturationcurve under its own vapour-pressure, the pressure is P_H+dP, $x=\xi$, $x_1=\xi_1$, $y=(y)_0+\eta$ and $y_1=(y_1)_0+\eta_1$.

In the points H and H_1 themselves the binary equilibrium $F+L+G$ exists; to this applies:

$$(y-\beta)\frac{\partial U}{\partial y}-U+\zeta=0 \qquad \frac{\partial U}{\partial y}=\frac{\partial U_1}{\partial y_1} \quad . \; . \; . \quad (8)$$

wherein the pressure is equal to P_H, $y=(y)_0$, $y_1=(y_1)_0$ and U and U_1 are independent of x and x_1.

We now take the condition (6), from this it follows:

$$RT\,log\,\frac{x_1}{x}=\frac{\partial U}{\partial x}-\frac{\partial U_1}{\partial x_1} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

Therefore, we obtain for very small values of x and x_1:

$$log\,\frac{\xi_1}{\xi}=\frac{1}{RT}\,Lim\left(\frac{\partial U}{\partial x}-\frac{\partial U_1}{\partial x_1}\right) \quad . \; . \; . \; . \; . \; . \quad (10)$$

or

$$\xi_1=K\,\xi \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

wherein K is determined in (10).

We now take the condition (7); in this we put the pressure P equal to P_H+dP, $x=\xi$, $x_1=\xi_1$, $y=(y)_0+\eta$ and $y_1=(y_1)_0+\eta_1$.

If we expand both terms of (7) into a series and consider that in the point H (8) is satisfied, then we find:

$$\left.\begin{array}{l} s\,\xi+t\,\eta+\dfrac{\partial V}{\partial y}dP+\frac{1}{2}\dfrac{\partial s}{\partial x}\cdot\xi^2+\frac{1}{2}\dfrac{\partial t}{\partial y}\cdot\eta^2+\frac{1}{2}\dfrac{\partial^2 V}{\partial y\partial P}dP^2+\dfrac{\partial s}{\partial x\partial y}\xi\eta+ \\ \qquad +\dfrac{\partial^2 V}{\partial x\partial y}\xi\,dP+\dfrac{\partial^2 V}{\partial y^2}\cdot\eta\,dP+\ldots[\;]_1 \end{array}\right\}(12)$$

Herein $r=\dfrac{\partial^2 U}{\partial x^2}$ $s=\dfrac{\partial^2 U}{\partial x\partial y}$ $t=\dfrac{\partial^2 U}{\partial y^2}$; these values must be kept, as they are in the point H. The second member of (12) is indicated by $[\;]_1$; this means that we deduce the second member from the first by substituting ξ_1, η_1, s_1, t_1 etc. for ξ, η, s, t etc. Now we expand (4) into a series; if we keep in mind, that in the point H (8) is again satisfied, and that x and x_1 must be put equal to zero, then we find a series, which we write in the following form:

$$RT\,\xi+\tfrac{1}{2}t\eta^2-(V-v)\,dP-\tfrac{1}{2}\left(\frac{\partial V}{\partial P}-\frac{\partial v}{\partial P}\right)dP^2+R+(y-\beta)\,L=0 \quad (13)$$

In R only terms occur, which are infinitely small with respect to those, which are already written down, viz. ξ^2, $\zeta\eta$, etc. $\xi\,dP$ and $\eta\,dP$ are wanting. L represents the first term of (12). For the sake of simplification (y_0) has been replaced by y.

If we expand (5) into a series, we find:

$$RT\,\xi_1+\tfrac{1}{2}t_1\eta_1{}^2-(V_1-v)\,dP-\tfrac{1}{2}\left(\frac{\partial V_1}{\partial P}-\frac{\partial v}{\partial P}\right)dP^2+R_1+(y_1-\beta)\,L_1=0 \quad (14)$$

Herein R_1 contains only terms, infinitely small with respect to those preceding, L_1 represents the second term of (12); $(y_1)_0$ has been replaced by y_1.

Now, in the point H the denominator of (8) (XI) is equal to zero, therefore:

$$(y_1-\beta)\,V+(y-y_1)\,v+(\beta-y)\,V_1=0.$$

We write this condition in the form:

$$\frac{V-v}{y-\beta}=\frac{V_1-v}{y_1-\beta}=\frac{V_1-V}{y_1-y}=\mu \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Now we have the four relations (11), (12), (13) and (14) between the five variables. If we multiply (13) with $y_1-\beta$ and (14) with $(y-\beta)$ then follows:

$$\left.\begin{aligned}(y_1-\beta)\left[RT\,\xi+\tfrac{1}{2}\,t\eta^2-\tfrac{1}{2}\left(\frac{\partial V}{\partial P}-\frac{\partial v}{\partial P}\right)dP^2\right]+\ldots=\\ =(y-\beta)\left[RT\,\xi_1+\tfrac{1}{2}\,t_1\eta_1{}^2-\tfrac{1}{2}\left(\frac{\partial V_1}{\partial P}-\frac{\partial v}{\partial P}\right)dP^2\right]+\ldots\end{aligned}\right\} \quad . \quad (16)$$

These equations may be satisfied when we take ξ and ξ_1 of the order dP^2 and η and η_1 of the order dP. From (12), (13) and (14) then follows:

$$t\eta+\frac{\partial V}{\partial y}dP=t_1\eta_1+\frac{\partial V_1}{\partial y_1}dP \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$t\eta=\left(\mu-\frac{\partial V}{\partial y}\right)dP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$t_1\eta_1=\left(\mu-\frac{\partial V_1}{\partial y_1}\right)dP \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

These last three equations are, as is seen immediately, dependent on one another. Substituting η from (18) and η_1 from (19) in (16 we find:

$$2\,RT\left[(y_1-\beta)-(y-\beta)\frac{\xi_1}{\xi}\right]\xi=a\,.\,dP^2 \quad . \quad . \quad . \quad (20)$$

Herein $\xi_1:\xi$ is fixed by (11); further is:

$$a=\frac{y-\beta}{t_1}\left(\mu-\frac{\partial V_1}{\partial y_1}\right)^2-\frac{(y_1-\beta)}{t}\left(\mu-\frac{\partial V}{\partial y}\right)^2+(y_1-\beta)\frac{\partial V}{\partial P}+(y-y_1)\frac{\partial v}{\partial P}+(\beta-y)\frac{\partial V_1}{\partial P} \quad (21$$

From (18) now follows:

$$2\,RT\left[(y_1-\beta)-(y-\beta)\frac{\xi_1}{\xi}\right]\xi=\frac{at^2}{\left(\mu-\frac{\partial V}{\partial y}\right)^2}\cdot\eta^2 \quad . \quad . \quad (22)$$

From (22) it follows that the saturationcurve under its own vapour-pressure under consideration is in the vicinity of the point H [fig. 4—6 (XI)] a parabola, which touches the side BC in H. From (18) and (20) follows the change of ξ and η along this curve at a small change of pressure dP.

We can find the meaning of a (22) in the following way.

We represent the length of Cp or Cq [fig. 1 (XI)] by Y, the length of the part, which is cut off by the liquid curve of the region $L - G$ from CB by y. Then we have:

$$t_0\frac{dY}{dP}=\frac{V_0-v}{Y-\beta}-\frac{\partial V_0}{\partial Y};\ t\frac{dy}{dP}=\frac{V_1-V}{y_1-y}-\frac{\partial V}{\partial y};\ t_1\frac{dy_1}{dP}=\frac{V_1-V}{y_1-y}-\frac{\partial V_1}{\partial y_1} \quad (23)$$

Herein t_0 and V_0 refer to the point of intersection of the saturationcurve with BC. Now we put:

$$Y-y=l$$

and we calculate $\frac{dl}{dP}$ and $\frac{d^2l}{dP^2}$. For this it may be considered that V_0 depends on P and Y, V on P and y and V_1 on P and y_1. If now the saturationcurve of F and the liquid-curve of the region $L - G$ go both through the point H, then (15) is satisfied; also at the same time V_0 becomes $= V$ and $t_0 = t$. Then we find:

$$\frac{dl}{dP}=0 \quad \text{and} \quad a=t\,(y-\beta)\,(y_1-y)\,\frac{d^2l}{dP^2} \quad . \quad . \quad . \quad . \quad (24)$$

Substituting this value of a in (20), we find after deduction with the aid of (13) (XI) and (11)

$$2\,RT\,.\,K\left(1-\frac{S}{S_1}\right)\xi=t\,(y-y_1)\,\frac{d^2l}{dP^2}\cdot dP^2 \quad . \quad . \quad . \quad (25)$$

and

$$2\,RT\,.\,K\left(1-\frac{S}{S_1}\right)\xi=\frac{t^3\,(y-y_1)}{\left(\mu-\frac{\partial v}{\partial y}\right)^2}\cdot\frac{d^2l}{dP^2}\cdot\eta^2\ . \quad . \quad . \quad (26)$$

wherein $t>0$; that there may be agreement with our figures, we take $y-y_1>0$.

We now distinguish two cases.

1. $1-\frac{S}{S_1}$ and $\frac{d^2l}{dP^2}$ have the same sign. From (26) it follows that ξ is positive, so that the parabola touches BC in H and is further situated within the triangle [fig. 6 (XI)]. This is apparent also yet from (25), as ξ becomes positive as well for dP positive as negative.

2. $1-\frac{S}{S_1}$ and $\frac{d^2l}{dP^2}$ have an opposite sign. From (26) it follows that ξ is negative. Therefore the parabola touches BC in H, but is further situated outside the triangle. Therefore a similar parabola may be imagined in fig. 5 (XI). Then only its point H represents a liquid, its other points have no meaning.

From our deduction of $\frac{dl}{dP}$ and $\frac{d^2l}{dP^2}$ in the point H, follows:

$$Y-y=\tfrac{1}{2}\cdot\frac{d^2l}{dP^2}\cdot dP^2.$$

Now, in the point H of fig. 4—6 (XI) $Y-y$, therefore also $\frac{dl^2}{dP^2}$ becomes positive, as well on increase as on decrease of pressure. When, however, the point H is situated on the other side of F, then $Y-y$ and therefore also $\frac{d^2l}{dP^2}$ becomes negative.

We now consider some cases.

1. F melts with increase of volume ($V>v$). $\frac{d^2l}{dP^2}>0$. S and S_1 positive.

a. $S>S_1$. From (26) follows: the saturationcurve under its own vapourpressure is a parabola, which touches BC in H, but is situated further outside the triangle [fig. 5 (XI)].

b. $S<S_1$. From (26) follows: the saturationcurve under its own vapourpressure is a parabola, which touches BC in H, but is further situated within the triangle. [fig. 6 (XI)].

2. F melts with decrease of volume ($V<v$). $\frac{d^2l}{dP^2}<0$.

We take again S and S_1 with opposite sign.

As sub 1. *a.* In fig. 5 (XI) the point H must be imagined on the other side of F, therefore, between F and B and H_1 between F and C.

From (18) it follows that η changes sign with dP, as in the point H the coefficient of dP is negative, η and dP must have the opposite sign. Therefore, the pressure increases in the direction in which η decreases and reversally. We see that this is in agreement with the direction of the arrows in fig. 5 and 6 (XI).

If it is desired to know the influence of a small change of T on the position of the saturationcurve under its own vapour pressure going through H, we must also include terms with dT in the previous expansions into a series. Now $U = Z - RTx \log x$ therefore, $\frac{\partial U}{\partial T} = - H - Rx \log x$, therefore in the point H $(x = 0)$ itself $\frac{\partial U}{\partial T} = - H.$

In the right member of (12), therefore, must be added $- \frac{\partial H}{\partial y} dT$ and terms with ξdT and ηdT; in the left member $- \frac{dH_1}{\partial y_1} dT.$

In (13) must be added $(H - \eta_v)\, dT$; in (14) $(H_1 - \eta_v)\, dT$; in order to distinguish the coördinate η, the entropy of the solid substance F is indicated by η_v.

In the first member of (16) must be added: $(y_1 - \beta)(H - \eta_v)\, dT$; in the second member $(y - \beta)(H_1 - \eta_v)$.

From (13) follows:

$$t\eta = \left(\mu - \frac{dV}{\partial y}\right) dP + \ldots$$

from (14)

$$t_1\eta_1 = \left(\mu - \frac{dV_1}{\partial y_1}\right) dP + \ldots$$

As we must substitute these values in (16), it is apparent that we may neglect the other terms. As

$$(\beta - y_1)\, H + (y_1 - y)\, \eta_v + (y - \beta)\, H_1 = (y - \beta) \frac{\Delta W}{T}$$

we obtain:

$$2\, RT \left[y_1 - \beta - (y - \beta) \frac{\xi_1}{\xi} \right] \xi = a \,.\, dP^2 + (y - \beta) \,.\, \frac{\Delta W}{T} \,.\, dT$$

or, after deduction:

$$2\, RT \,.\, K \left(1 - \frac{S}{S_1}\right) \xi = t\, (y - y_1) \frac{d^2 l}{dP^2} \,.\, dP^2 - \frac{\Delta W}{T} dT \quad . \quad . \qquad (27)$$

and:

$$2\, RT \,.\, K \left(1 - \frac{S}{S_1}\right) \xi = \frac{t^3\, (y - y_1)}{\left(\left(\mu - \frac{\partial V}{\partial y}\right)^2\right.} \,.\, \frac{d^2 l}{dP^2} \,.\, \eta^2 - \frac{\Delta W}{T} \,.\, dT \quad . \qquad (28)$$

From (28) it follows that not only the saturationcurve under its own vapour-pressure, going through H, but also those which are situated in the vicinity of H are parabolas.

In the point H of figs. 5—6 (XI) ΔW is negative, when H is situated on the other side of F, ΔW is positive. From (28) it now follows:

when the curve, touching in H is situated outside the triangle [fig. 5 (XI)], it shifts on decrease of T, within the triangle [curve hn in fig. 5 (XI)]

when the curve, touching in H is situated within the triangle [fig. 6 (XI)], it shifts on increase of T within the triangle [the closed curve in fig. 6 (XI)] and on decrease of T partly outside the triangle. Therefore, curve hn of fig. 6 (XI) must be imagined to be closed by a part hn situated outside the triangle; this part, however, has no physical meaning.

In fig. 1 three curves are drawn through F; Fl is the liquidcurve of the region L—G at the temperature T_F and under the pressure P_F, therefore at the minimummeltingpoint of F; FK is the boilingpointcurve and Fs the saturationcurve under its own vapourpressure. The two first curves are but partly drawn. We now construe in F a tangent to each of these curves. With the aid of the formulas from the previous communication, we find:

for the tangent to the liquidcurve (Fl) of the region LG:

$$\left(\frac{dy}{dx}\right)_l = -\frac{\left(\frac{x_1}{x}-1\right)RT+(y_1-\beta)s}{(y_1-\beta)\,t} \quad . \quad . \quad . \quad . \quad (29)$$

for the tangent (FZ_1) to the boilingpointcurve (FK):

$$\left(\frac{dy}{dx}\right)_k = -\frac{\left(\frac{x_1}{x}-1\right)RT+(y_1-\beta)s-RT\frac{D}{B}}{(y_1-\beta)\,t} = \left(\frac{dy}{dx}\right)_l + \frac{D}{B}\cdot\frac{RT}{(y_1-\beta)t} \quad (30)$$

and for the tangent (FZ_2) to the saturationcurve under its own vapourpressure (Fs):

$$\left(\frac{dy}{dx}\right)_s = -\frac{\left(\frac{x_1}{x}-1\right)RT+(y_1-\beta)s-RT\frac{C}{A}}{(y_1-\beta)\,t} = \left(\frac{dy}{dx}\right)_l + \frac{C}{A}\cdot\frac{RT}{(y_1-\beta)\,t} \quad (31)$$

Now we take again the most probable case that BC—AD is positive (communication II). That there may be agreement with the figs. 5 and 6 (XI) and fig. 1, we take $V > v$ therefore A positive. As further y_1—β is negative, we can deduce:

$$\left(\frac{dy}{dx}\right)_l > \left(\frac{dy}{dx}\right)_k > \left(\frac{dy}{dx}\right)_s \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The curves Fl, Fk and Fs must, therefore, be situated with respect to one another as in fig. 1.

When $V < v$, therefore A is negative, then it follows:

$$\left(\frac{dy}{dx}\right)_s > \left(\frac{dy}{dx}\right)_l > \left(\frac{dy}{dx}\right)_k \quad . \; . \; . \; . \; . \; . \; . \quad (33)$$

The point H and therefore also the point s, must be imagined, however in this case, also in fig. 1 on the other side of F. In agreement with (33) Fl comes then between the two other curves.

Now we shall consider the solutionpath consisting of a straight line of F under its own vapourpressure or in short the solutionpath of F. We take viz. the system $F + L + G$, but we take care that the quantity of vapour is always very small. On change of T the liquid traces a straight line going through F, which we have called the solution- or cristallisationpath of F. In fig. 1 three similar solutionpaths FZ, FZ_1, and FZ_2 are drawn.

Let us consider now the binary equilibrium $F + L + G$. In fig. 2 its P,T-curve is represented by EFU, Q is the point of maximumpressure, H the point of maximumtemperature; F is the minimummeltingpoint, K the point of maximumsublimation of the compound. aK is the sublimation-, Fd the meltingcurve. Curve EFU touches Fd in F and aK in K. It is apparent from the direction of the meltingcurve that we assume $V > v$ in agreement with fig. 1.

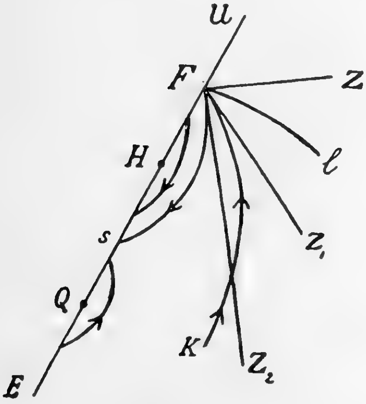

Fig. 1.

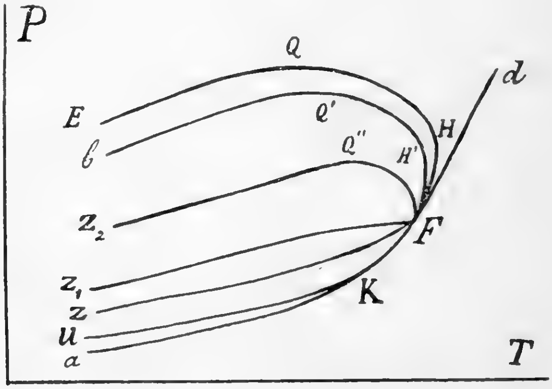

Fig. 2.

When the solutionpath FZ in fig. 1 coincides with FU, its P,T-curve in fig. 2 is, therefore, represented by UKF; when FZ coincides in fig. 1 with FE, it is represented in fig. 2 by EHF. When the solutionpath FZ in fig. 1 turns from the position FU

towards FE, its corresponding P,T-curve must therefore change from UKF into EHF. Now we shall examine this more in detail.

The saturationcurves under their own vapourpressure have, in the vicinity of H either a form as in fig. 5 (XI) or as in fig. 6 (XI); we assume that they have a form as in fig. 5(XI). In fig. 1 the curve surrounded by Fs, and Fs, itself represent saturationcurves under their own vapourpressure; the arrows indicate the direction of increasing pressure.

The boilingpoint curves have also a position as in fig. 5 (XI); we must consider, however, that H is replaced by the point of maximumpressure Q and that the arrows point in opposite direction. Two of these curves are drawn in fig. 1, one in the vicinity of Q and curve Fk; the latter is indicated for a part only.

Now we imagine in fig. 1 a solutionpath between FE and FZ_2. Imagining in this figure still many other saturation-curves under their own vapourpressure to be drawn, then we see that some of these are not intersected by this path, other ones twice, and others again once. Further we see that one of these curves touches this path; we call that point of contact H'.

From this it follows: at first the temperature increases along this solutionpath from F up to H' and after that it decreases. Further it follows: $T_{H'}$ is lower than T_H.

Imagining yet many other boilingpoint-curves to be drawn in fig. 1, then we see that one of these touches the solutionpath in a point that we shall call Q'. Now we deduce: the pressure increases along this solutionpath from F up to Q' and after that it decreases. Further it follows: $P_{Q'}$ is smaller than P_Q.

Now it follows from this all that the P,T-curve belonging to this solutionpath has a form in fig. 2 as curve bF with a point of maximumpressure in Q' and a point of maximumtemperature in H'.

As long as the solutionpath in fig. 1 is situated between FE and FZ_2, the P,T-curves retain a form as bF in fig. 2; according as the path, however, approaches closer to FZ_2, the points Q' and H' come closer to F. When the path coincides with FZ_2, H' coincides with F and the P,T-curve has a form as Z_2F in fig. 2 with a point of maximumpressure Q''. The tangent in F stands vertically.

To see this, it must be considered that the line FZ_2 touches in F the saturationcurve under its own vapourpressure going through F (Fs in fig. 1). Going from F, along an infinitely small distance, along curve Fs and therefore also along the tangent FZ_2, the pressure increases while the temperature remains constant. As dP, therefore, is positive, and dT is zero, the P,T-curve therefore, in fig. 2, along a small distance, must point vertically upwards, so that it has there a vertical tangent. Considering the saturationcurves under their own vapourpressure, we see that FZ_2 intersects only curves of temperatures lower than T_H, so that the temperature decreases along FZ_2 from F.

Considering the boilingpointcurves, we see that the same still applies to these as to a solutionpath, situated between FE and FZ_2. The pressure, therefore, increases at first from F and after that it decreases. From all this it follows that the P,T-curve has, therefore, a form as curve bF in fig. 2.

Let us now take a solutionpath between FZ_1 and FZ_2. It is easy to see that the P,T-curve retains a form as FZ_2 in fig. 2, with this difference, however, that the tangent in F stands no longer vertically. The curve proceeds viz. from F immediately towards higher pressures and lower temperatures. According as the solutionpath in fig. 1 comes closer to FZ_1, in fig. 2 the point of maximumpressure Q'' approaches closer to F. When the solutionpath coincides with FZ_1, Q'' coincides with F, and in figure 2 the P,T-curve obtains a form as Z_1F with a horizontal tangent in F.

In order to see this, we consider the solutionpath FZ_1 which touches the boilingpointcurve FK in F. (fig. 1). Going from F along an infinitely small distance along curve FK and, therefore, also along the tangent FZ_1, the temperature decreases, while the pressure remains constant. As dT, therefore, is negative and dP is zero, the P, T-curve must, therefore, from F over a small distance point horizontally towards the left; consequently it has a horizontal tangent in F.

We now take a solutionpath FZ, situated between FU and FZ_1. It follows from a consideration of the saturationcurves under their own vapourpressure and the boilingpointcurves in the vicinity of F, that pressure and temperature decrease from F. The P, T-curve is represented in fig. 2 by FZ, it proceeds from F towards lower temperatures and pressures.

At the deduction of fig. 2 it is assumed that the saturationcurves under their own vapourpressure and the boilingpointcurves have a form as in fig. 1. Curve Fs and Fk are drawn herein in the vicinity of F, concave towards H. When in F they turn their convex side towards H, then curve Fs will intersect its tangent FZ_2 still in another point and curve FK its tangent FZ_1. Although then in fig. 2 the tangent in F to Z_1F remains horizontal and the tangent to Z_2F vertical, all curves will obtain a somewhat different form in the vicinity of F (we may also compare the previously treated P, T diagrams for the case that F is a ternary compound).

After the previous considerations, the reader can easily deduce the P, T diagram for the solutionpaths of F, when the curves are situated as in fig. 6 (XI).

Formerly [5 (IV)] we have deduced for a solutionpath

$$\frac{dP}{dT}=\frac{DM-BN}{CM-AN} \quad \ldots\ldots\ldots \quad (34)$$

now, as $a=0$, herein is:

$M=x^2 r+2 x (y-\beta) s+(y-\beta)^2 t$

$N=x (x_1-x) r+[x (y_1-y)+(x_1-x) (y-\beta)] s+(y_1-y) (y-\beta) t$

In the point F becomes $x=0$ and $y=\beta$, therefore $M=0$ and $N=0$. Let us now contemplate a solution path and let us call the angle, which it forms with the X-axis, φ. If we imagine for the sake of simplicity that the coordinatesystem is rectangular, then it follows: $cotg.\ \varphi=x:(y-\beta)$. We then obtain:

$$\frac{M}{N}=\frac{x\, r\, cotg\, \varphi+2\, x\, s+(y-\beta)\, t}{(x_1-x)\, r\, cotg\, \varphi+[(y_1-y)\, cotg\, \varphi+x_1-x]\, s+(y_1-y)\, t}$$

In the point F becomes $x=0$ and $y=\beta$ therefore:

$$\frac{M}{N}=\frac{RT}{\left(\frac{x_1}{x}-1\right) RT+(y_1-\beta)\,(s+t\, tg\, \varphi)} \quad \ldots \quad (35)$$

The question now arises, what P, T curve touches the meltingline Fd in F. For this must, according to (34):

$$\frac{DM-BN}{CM-AN}=\frac{B}{A}$$

therefore, $M:N=0$. It is apparent from (35) that this is only the case when $tg\ \varphi$ is infinitely great, consequently for $\varphi=90°$ and $\varphi=270°$. Then the solutionpath coincides either with FE or with FU (fig. 1). Therefore, both the binary solutionpaths EF and UF only touch in F the meltingline Fd; the ternary paths do not touch this meltingline.

In order that the tangent to the P, T curve of a solutionpath may be vertical in F we have, according to (34) $CM-AN=0$. As $M:N$ is fixed by (35), it follows that this is the case, when

$$tg\, \varphi=-\frac{\left(\frac{x_1}{x}-1\right) RT+(y_1-\beta)\, s-RT\, \frac{C}{A}}{(y_1-\beta)\, t}$$

From (31) it follows that in F this solutionpath must touch the saturationcurve under its own vapourpressure going through the point F [curve Fs fig. 1], the required solutionpath is, therefore, FZ_2.

If we require a solutionpath, whose P,T curve has a horizontal tangent in F, we must, as follows from 34) put $DM-BN=0$. From this now follows:

$$tg\,\varphi = -\frac{\left(\frac{x_1}{x}-1\right)RT+(y_1-\beta)\,s-RT\,\frac{D}{B}}{(y_1-\beta)\,t} \quad . \; . \; . \; . \quad (37)$$

From this it follows, in connection with (30) that in F the solutionpath must touch the boilingpointcurve going through the point F [curve Fk in fig. 1]; the wanted solutionpath is, therefore, FZ_1.

Now it follows from the previous considerations: in the P,T diagram (fig. 2), none of the ternary solutionpaths touches the meltingline Fd in F; the solutionpath, touching in F in the concentrationdiagram (fig. 1) the saturationcurve under its own vapour-pressure going through F, has in the P,T diagram a vertical tangent in F; the solutionpath, in the concentrationdiagram touching the boilingpointcurve going through F, has a horizontal tangent in F in the P,T diagram.

It is evident that the above-mentioned rules apply quite generally no matter whether the relations of fig. 5 (XI) or 6 (XI) occur or the curves in F are concave or convex towards H.

In fig. 1 Fl represents the liquidcurve of a region LG, now we imagine a solutionpath, touching curve Fl in F. The direction of this solutionpath is, therefore, fixed by (29). In order to find $\frac{dP}{dT}$ in the point F of this path, we must, therefore, substitute the second term of (29) in (35) for $tg\varphi$. We then find an infinitely great value for (35). From (34) now follows:

$$\frac{dP}{T}=\frac{D}{C}=\frac{H_1-H+(\beta-y_1)\,\frac{\partial H}{\partial y}}{V_1-V+(\beta-y_1)\,\frac{\partial V}{\partial y}} \quad . \; . \; . \; . \quad (38)$$

The latter part of (38) indicates the direction of the P,T-curve of the evaporationline of the liquid F. This line is traced, when we melt the substance F and when we regulate after that the temperature and the pressure in such a way that the liquid remains in equilibrium with an infinitely small quantity of vapour. Therefore the liquid retains the composition F during this. This curve is represented in fig. 3 (III) by Fe, the pressure and the temperature increase from F along this curve.

Consequently we find: the solutionpath, touching in F in the concentration-diagram the liquid curve of the region L-G (curve Fl in fig. 1) going through F, has in the P,T-diagram the same tangent in F as the evaporationline of the liquid F starting from F.

If we compare the P,T-diagram of the solutionpaths of a binary compound F (fig. 2) with those of a ternary compound F [fig. 4 (IV) and 1 – 3 (V)], then we see very great differences in the vicinity of the point F. We find these differences also in the concentration-diagrams. When viz. in fig. 1. in the point F we construct tangents to the curves Fl, Fk and Fs going through the point F, three different tangents arise. If F is a ternary compound, as e. g. in fig. 1 (IV), then these curves touch one another in F and the three tangents coincide in the line XFY.

All this is based on the following. When F is a binary compound, a new substance must be added, in order to trace a ternary solution-path from F. When, however, F is a ternary compound, we add no new substance in order to trace a solutionpath, from F, but substances, which are already present in the melted F.

(*To be continued*).

Physics. "*An apparatus for the determination of gas isotherms up to about* 3000 *atms.*" Van der Waals-fund researches N°. 5. By Prof. Ph. Kohnstamm and K. W. Walstra. (Communicated by Prof. van der Waals).

(Communicated in the meeting of December 27, 1913).

As is known the material for testing the theory of the equation of state at very high pressures consists almost exclusively of what Amagat has published in his famous papers. It seems desirable for different reasons to extend this material. Quite apart from the desirability to get to know the behaviour of other gases than those examined by Amagat — we think in the first place of the mon-atomic gases — Amagat's work itself gives rise to different questions, which can only be decided by means of new experiments.

First of all it is known that Amagat does not give the direct results of his observations; he only publishes the results of a graphical interpolation between these observations. The question rises how great the deviations are between the interpolated and the real observations, and whether another way of interpolation had been possible. Nor can the probable experimental error of Amagat's observations be inferred from his experiments. And it has finally appeared that there are discrepancies between some of **Amagat**'s results inter se, as well as between **Amagat**'s observations on hydrogen at high pressures on one side, and **Schalkwijk**'s very accurate observations for low pressures on the other side[1]).

For all these reasons it seemed desirable to construct an apparatus with which gas-isotherms might be measured up to the highest attainable pressures. And as it is self-evident that the cost of such a set of apparatus could not be defrayed from the ordinary means of a laboratory, the board of the van der Waals-fund resolved already in 1904 to grant money for this purpose. It is owing to the strong support given by the van der Waals-fund all these years that we are now able to communicate the first results. Our cordial thanks are due to the board of the van der Waals-fund, and further to all who helped to support the fund.

In the following pages we shall of course not give an account of all the difficulties that confronted us, and the way in which they were finally surmounted. We shall confine ourselves to a description of the arrangement in its present form, and only mention in a few words now and then what considerations have led to this final form. We shall successively discuss the measurement of the pressure, the volume, and the temperature.

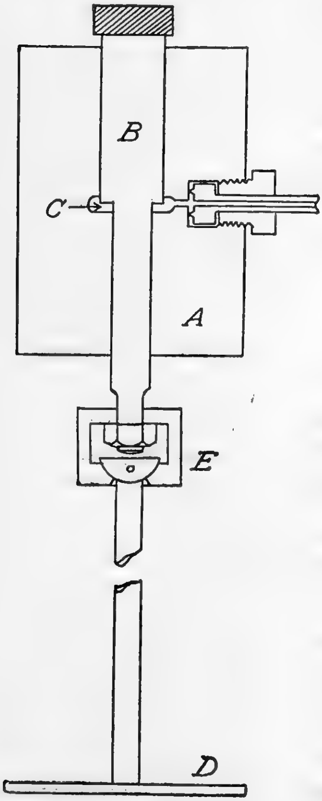

Fig. 1.

A. *Measurement of the Pressure.*

The measurement of the pressure in absolute measure takes place by means of **Schäffer** and **Budenberg**'s pressure balance. In principle this apparatus consists of a steel piece *A* (fig. 1) with cylindric boring, which at about half the height passes into a wider cylindric boring. A differential piston *B* fits in this boring, which piston is ground into the two cylindres with the utmost care. By means of a side tube the cavity *C* can be connected with the space where the pressure is to be measured. This side tube and the space under the piston are filled with machine oil. By means of a mould,

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[1]) **Brinkman**, Thesis for the Doctorate, Amsterdam p. 34.
Schalkwijk. Thesis for the Doctorate, Leiden 1908, p. 120 et. seq.
Keesom. Thesis for the Doctorate, 1904, p. 57.

which has been prepared and measured with the utmost care, the two apertures in the steel piece A and the two sections of the cylindre B are ground in such a way that the difference between the larger and the smaller section has a definite size, e.g. 1 cm^2. If we now suppose a pressure e.g. of 800 kg. per cm^2 to prevail in the space C, and no friction to be present, the piston B would be forced upwards with a force of 800 kg. If on the plate D, which is connected with B by means of the socket joint E we put so many weights that they together with B, D, E and the joining-rod F weigh exactly 800 kg., the whole apparatus is exactly in equilibrium. If the total weight amounts to 801 kg. — we still suppose absence of friction — the piston descends till the liquid in C and the space in connection with it is compressed so much that there prevails a pressure of 801 kg. per cm^2 in C. If the total weight amounts to 799 kg., the piston rises till the pressure in C has fallen to 799 kg. per cm^2. On account of the strong friction of the piston very tightly fitting in the cylindre nothing, however, is to be observed of these movements. In fact the plate D can easily be loaded with 10 or 20 kg. too much or too little without any movement being perceived on a manometer connected with C. If, however, the piston B with the plate D and all the weights lying on it are made to rotate round their axis, it appears that this rotation has practically annihilated all the friction. It will appear from the description of our experiments that the remaining friction will lie far below 10 gr. at low pressures, and that it can certainly not be so much as 50 gr. for pressures of 2500 kg.

We cannot account for this most remarkable property, though it is of course clear that the fact that C is filled with machine oil, and that this oil penetrates between piston and cylindre wall plays an important part in this. It is known that also in AMAGAT's manometer the great decrease of friction when the piston moves with respect to the cylindre wall is utilized. But in AMAGAT's manometer ¹) the piston must be moved to the left and the right by hand, also during the measurement. The mode of construction of SCHÄFFER and BUDENBERG's pressure balance evades this by making the whole mass of the weights, for the large model up to 1250 kg., for the small one up to 250 kg. rotate with the piston B. After these

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¹) This manometer is generally called after DESGOFFE; according to AMAGAT, however, the first idea came from GALLY—CAZALAT. And we owe to AMAGAT the great improvement, which rendered the instrument for the first time adapted for really accurate measurements, nl. the free movability of the pistons.

weights have once been set rotating by the hand or in another way, the apparatus may be left to itself. The kinetic energy of the rotation is so great that the apparatus continues rotating for a considerable time, at any rate long enough to perform a pressure measurement. Only on account of this circumstance it is possible fully to avail oneself of the absence of friction in consequence of the rotation, for it appears that any, also the lightest, touch of the apparatus brings about increase or decrease of the pressure in *C*, as it is not possible in doing so not to exert a force on the piston *B* in vertical direction. If the space *C* is connected with a sensible manoscope (and the volumemeter itself served as such in our experiments) every touching of the piston, also the slightest, betrays itself immediately by a deviation of the manoscope. Measurements may, therefore, only be made when the apparatus is in rotation, and entirely left to itself.

A second circumstance, on account of which in our opinion SCHÄFFER and BUDENBERG's pressure balance may claim to be considered as an improvement compared with AMAGAT's manometer, is this that the differential piston as well as the cylindre consist of one piece, and can therefore be completely finished as a whole on the lathe. As is known AMAGAT's manometer makes use of two pistons of different section, which are connected with each other. In the vessel where the great pressure which is to be measured, prevails, there is a small piston, accurately ground in, and the force with which it is expelled is transmitted to a large piston, which can move in a second vessel; the pressure in this latter vessel is measured by means of mercury. In this construction it is, however, not to be avoided that the axes of the two pistons are not entirely each other's prolongation, which must give rise to wrenchings and frictions. To prevent these the pistons must, of course, not be so tightly ground in as would otherwise be possible. It is known that AMAGAT therefore uses molasses as transmission liquid in his manometer, because else the transmission liquid would flow away too quickly, whereas in SCHÄFFER and BUDENBERG's pressure balance thin machine oil suffices.

On the other hand SCHÄFFER and BUDENBERG's pressure balance shares a drawback with AMAGAT's manometer, which as far as I know, WAGNER [1]) was the first to point out in his investigation of an AMAGAT manometer. AMAGAT himself took as effective area of the piston, i. e. as area on which the pressure acts to the outside, simply the section of the piston itself. WAGNER, however, points out that the liquid which is pressed through between piston and cylindre

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[1]) Thesis for the Doctorate. München 1904. Ann. d. Phys. (4) 15, p. 906.

wall exerts a friction force on the cylindrical surface of the piston, and that in consequence of this the force which drives the piston out must really be greater than the amount which can be calculated from the section of the piston and the pressure. Or in other words the effective area of the piston must be greater than the real section. By means of hydro-dynamic considerations WAGNER now comes to the conclusion that the difference will depend on the width of the cylindre in which the piston moves. Half the difference between piston and cylindre section will namely have to be added to the piston section to determine the true effective area. Hence WAGNER did not only very accurately determine the piston section, as AMAGAT did, but also the cylindre diameters (at least for the two small steel pistons which he used). The difference between the two diameters amounted to about 0,01 mm.; it is therefore by no means insignificant for a total amount of about 5 mm.

WAGNER has, however, also determined the effective area by a direct experimental way, by namely ascertaining with what weights the pistons must be loaded to balance a pressure which is directly measured by means of a mercury column. And he then arrives at a very remarkable result. For whereas the measurement yielded 5,128 resp. 4,076 mm. for the piston diameters, 5,138 resp. 4,088 for the cylindre diameters, which according to the above would give 5,133 resp. 4,082 for the effective area, the direct experimental equation yielded 5,127 resp. 4,076, i. e. exactly the sections of the pistons without any correction. Evidently WAGNER has not pointed this out, because in his first investigation the direct experimental determination of the effective area of the large piston of the AMAGAT-manometer yielded 40,189, whereas the section of the piston itself amounted only to 40.176.[1]). In a later investigation, however, which was undertaken in collaboration with P. P. KOCH[2]), WAGNER repeated these determinations. He now finds in measurements which he considers more accurate than the earlier ones again 5,128 for the effective area of the small piston, but 40.164 for that of the large one, i. e. even a little less than the real section. Accordingly these determinations cannot give support to the theory of the increase of the effective area in consequence of the friction on the cylindrical surface derived hydrodynamically. [3])

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[1]) l.c. p. 919.

[2]) Ann. d. Phys. (4) 31, p. 48.

[3]) Some particulars in BRIDGMAN's interesting experiments (Proc. Amer. Acad. XLIV p. 201) seem to point in the same direction, but whether this supposition is true cannot be inferred from the communication with certainty. We shall, therefore, not enter any further into this.

This question which is of fundamental importance for all absolute pressure measurement, cannot be considered as decided as yet. Nor can our experiments at this moment give a decision, because we have not yet been able to compare one of our pressure balances directly with an open manometer with transmission for sufficiently high pressures (60 to 100 atm.). The indirect comparison obtained by the very close agreement of our hydrogen-isotherm with that of SCHALKWIJK, seems to point in the same direction as WAGNER's experiments, that namely actually effective and real area coincide. Nevertheless a direct comparison remains, of course, a matter of the highest importance for all our measurements and we greatly hope, therefore, to be able to carry out a comparison before long.

In what precedes we have discussed the principle of SCHÄFFER and BUDENBERG's pressure balances. We should now discuss for a moment the execution of it in practice. For the lower pressures — up to 250 atm. — this is very simple indeed. The cylindre A (fig. 2) rests on a heavy cast tripod, which again is supported on a stand,

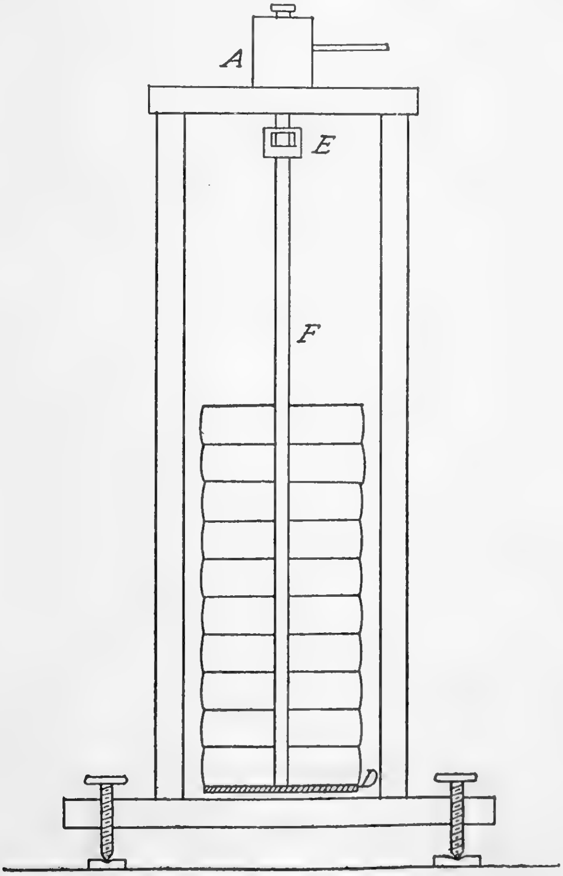

Fig. 2.

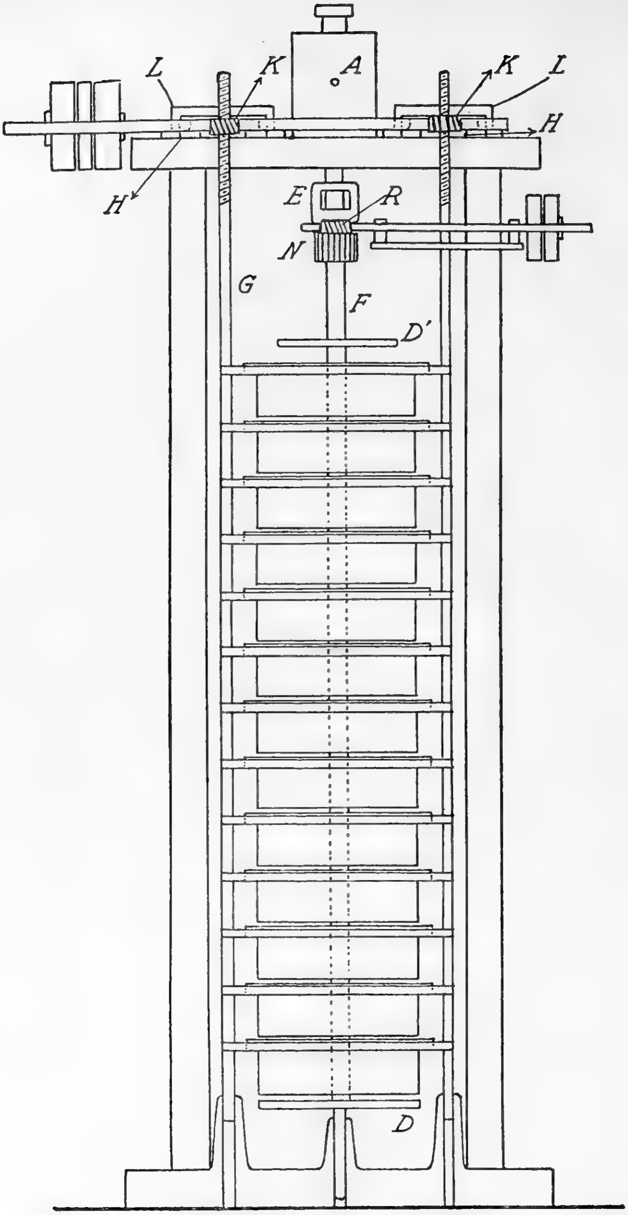

Fig. 3.

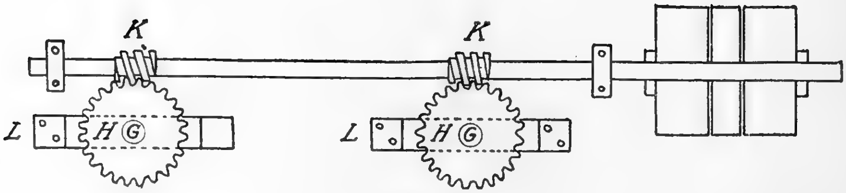

Fig. 3*a*.

which can be put in the required position by means of adjusting screws. On the plate *D* an iron weight is placed, weighing with *B*, *E*, *F*, and *D* together exactly 25 kg. Then plate-shaped weights of 25, 10 etc. to 1 kg. and lower are put on it with a slit, which enables them to slide round the rod *F*. The whole apparatus is set rotating by hand.

For higher pressures the gauge cannot be worked solely by the hand. The "head" of the pressure balance (the piece *A* with the piston *B*, fig. 1) is mounted here on an iron stand 2 m. high, which by accurate levelling has been adjusted, and rests on a separate heavy stone foundation. Weights of 100 kg. lie round the rod *F* (fig. 3) in rings, on which they rest. These rings are connected by means of two bars *G* and the distances between the rings are taken so that between two weights there always remains a space of 2 cm.

The rods *G* are provided at their upper ends with screw thread, and are in this way carried by the nuts *H* (fig. 3*a*) [1]), which rest on the top plate of the iron stand, and are fixed by bent pieces *L*. The nuts *H* are provided on the outside with teeth, in which a worm *K* catches. By means of this the nuts *H* can be turned, and in this way the rods *G* and all the rings attached to them can be adjusted higher or lower. When the rods are turned down, first the lowest weight will get to lie on the plate *D*; this weight has been taken so that together with the plate *D*, the rods *F* and *E*, and the piston it weighs exactly 100 kg. If the rods *G* are turned still lower down, another weight of exactly 100 kg. will rest on this weight etc. In this way the piston can in all be loaded with 1150 kg. If the worm is turned in the opposite direction, the ring-system rises, and lifts up the weights one after another, which relieves *D*. By means of a transmission with two loose pulleys and a fast pulley the worm is driven from a shaft, which in its turn is set going by an electromotor of 1 H.P. Two belts run over the loose pulleys, a crossed one and a straight one. By a simple adjusting apparatus either the one or the other can be transferred to the interjacent fast pulley, by which weights are put on or taken off. Smaller weights are put on by the hand on the plate *D'*, which is fastened on the rod *F*.

In the second place it is necessary to get a mechanical arrangement to set the pressure balance rotating. For this purpose a toothed wheel *M* [2]) (Fig. 3*b*) has been fixed on the rod *F*, which engages

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[1]) Fig. 3*a* gives a view from below, omitting the plate on which everything rests. In Fig. 3 the nuts *H* are hidden behind the worm *K* and the rod on which it is fastened.

[2]) In Fig. 3 *M* is hidden behind *N*.

a second toothed wheel *N*. *M* is about 32 mm. high, *N* only 23 mm. This is necessary because the toothed wheel *N* is rigidly adjusted at a fixed height, whereas *M* moves up and down with the rod *F*, and therefore with the piston *B* in the cylindre *A*, for so far as the cylindre *A* leaves room for it, i.e. about $2^1/_2$ cm. The toothed wheels *M* and *N* must be able to engage each other at every position made possible by the space left.

By the plate *O* turning round *P*, *N* can now be put in two positions: so that its teeth catch in *M*, and so that the two toothed wheels are clear of each other. When once the weights have been well set rotating, *N* is placed in the latter position, and fixed, so that the toothed wheels no longer catch into each other, and the piston *B* therefore with the weights attached to it rotates perfectly freely, and no other forces act on it than gravity and the pressure of the liquid. *N* is driven by the worm *R*. The latter receives its motion by means of a transmission with fast and loose pulleys from the shaft, which is set going by the electromotor. To prevent the toothed wheels from breaking, or connections from being strained when the belt should be transferred from the fast to the loose pulley, the toothed wheels catching into each other and the weights being in strong rotation, *N* is provided with a free-wheel *S*, as is also in use for bicycles. It is therefore possible by setting the worm in motion, to make *N* and with it *M* and the weights rotate, but a rotation of *M* only sets *N*, and not the worm going.

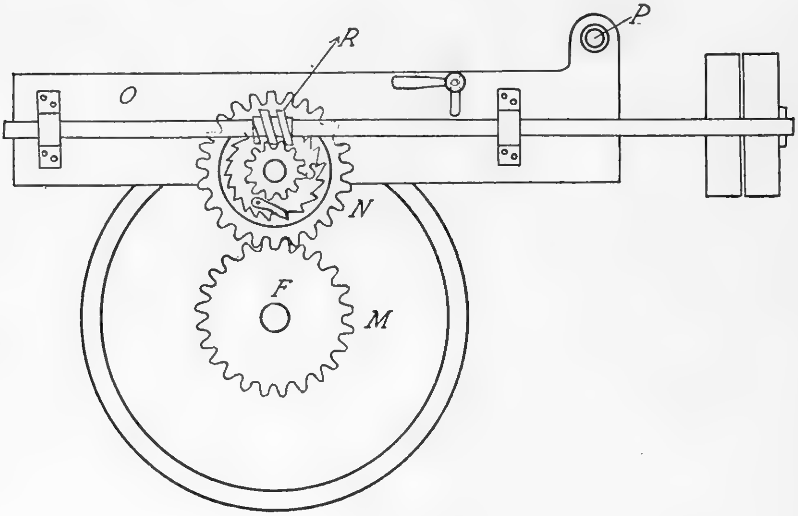

Fig. 3*b*.

It is self-evident that the pressure indicated by the pressure balance, is the pressure at C (fig. 1). The pressure at the place where one wants to know it, in casu at the place where the isotherm measurements take place, must be derived from that in C by means of a correction for the hydrostatic pressure difference in C and the first-mentioned place.

The measurement of the pressures above 1250 kg. takes place in exactly the same way, only then the "head" A is exchanged for another cylindre and piston whose effective area is only $^1/_4$ cm.^{2} instead of 1 cm^2. With this "head" therefore pressures of 5000 Kg. per cm^2 might be attained. The firm SCHÄFFER and BUDENBERG, however, informed us in 1906 when they prepared the apparatus, that already at about 4000 atm. a permanent change of form of the cylindre A was to be feared in consequence of a transgression of the limit of elasticity of the steel, so that this pressure could not be exceeded for the pressure balance. Since then BRIDGMAN has succeeded in far exceeding this limit of pressure by means of apparatus of newer kinds of steel. The question, however, remains whether his apparatus could be modified for the determination of gas isotherms. Apart from the much greater complexity and dimension of the apparatus also the question of a transmission liquid which could be used in the absolute pressure gauge, is to be considered. The machine oils, which we always used as transmission liquid in the following investigations, because they best remove the friction between the cylindre and piston, begin to be so viscous already at room temperature and 3000 atm., that the pressure gauge begins to be slow in its indications, and also the transmission of the pressure in the narrow channels becomes highly uncertain. For this reason we have for the present confined ourselves to pressures below 3000 atm.

The very great value of the viscosity of the mineral oils at high pressures is ascribed by TAMMANN and BRIDGMAN to the solidification of these substances. With the apparatus, however, described in N°. 4 of these communications (These Proc. XV p. 1021) nothing is to be perceived of a deposition of solid substance at these pressures. The oil remains as transparent when this pressure is approached as it was at first, nor is anything to be observed of crystallisation. We have, therefore, only to do with a very viscous fluid, possibly a continuous transition into an amorphous solid phase.

B. The volume measurement.

For the measurement of volume we have made use of a somewhat modified method of the electric contacts. Just as with AMAGAT, platinum wires about 1 mm. thick were originally sealed into a glass tube. It appeared, however, that such sealing places were no longer to be trusted after the tube had been compressed to e. g. 2500 atm. Sometimes they lasted some time longer, often however they already came forth cracked from the pressure apparatus, and in any case the reliability was exceedingly slight. Amagat too complains of the great fragility of his tubes. An investigation undertaken specially for this end showed that the cause of the phenomenon will be found in the difference of compressibility between enamel glass and platinum, in consequence of which the connection between the wire and the glass is lost at high pressures.

This gave an indication of the way in which improvement was to be expected. If only the platinum wires are taken exceedingly thin, the change of volume cannot be so great that detaching is to be feared. Glass tubes in which capillary wires of 0.0356 mm. of Hartmann and Braun were sealed, appeared really not to lose anything of their strength, not even when they had been kept at 3000 atm. for a long time. It is, however, not possible to seal in these wires in such a way that the mercury forms contact against a loose point of them; it is self-evident that they are too limp for this. This difficulty can be overcome by not letting a bit of wire stick out in the tube, but by sealing in the wire at both its extremities. The whole tube is therefore made as follows. A thick-walled capillary tube of Jena enamel glass is blown out to small reservoirs in 15 or 20 places. At the top there is a somewhat larger reservoir, above which the tube is drawn out to a very narrow capillary. Under the said widening there are a number of very small reservoirs, which pass into reservoirs that become gradually larger, to distribute the points as uniformly as possible over the isotherm that is to be determined. Now the tube is cut through at the places between the reservoirs, which have kept their normal thickness of wall; a platinum wire of the said strength is laid between the two ends, so that the wire projects outside on either side, and then the glass is fused together again. In this the wire is bent downward in a point to get a sharper contact with the mercury. Then the projecting ends are connected with a spiral of the same platinum wire, which is attached to the tube by means of "zapon"-lac and gelatin. (See Fig. 4. For clearness' sake the wire is drawn beside the tube. Fig. 5 gives the real position). If the mercury is quite at the bottom of the tube, the resistance between the two leads is the total amount of the platinum spiral, e. g. 150 Ohms. As soon, however, as the mercury has risen to the second contact B, the resistance AB e. g.

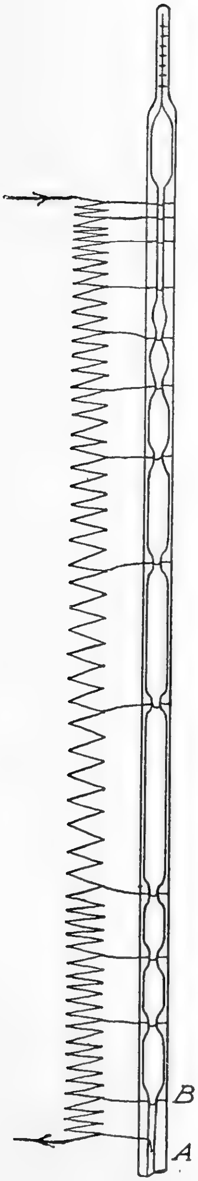

Fig. 4.

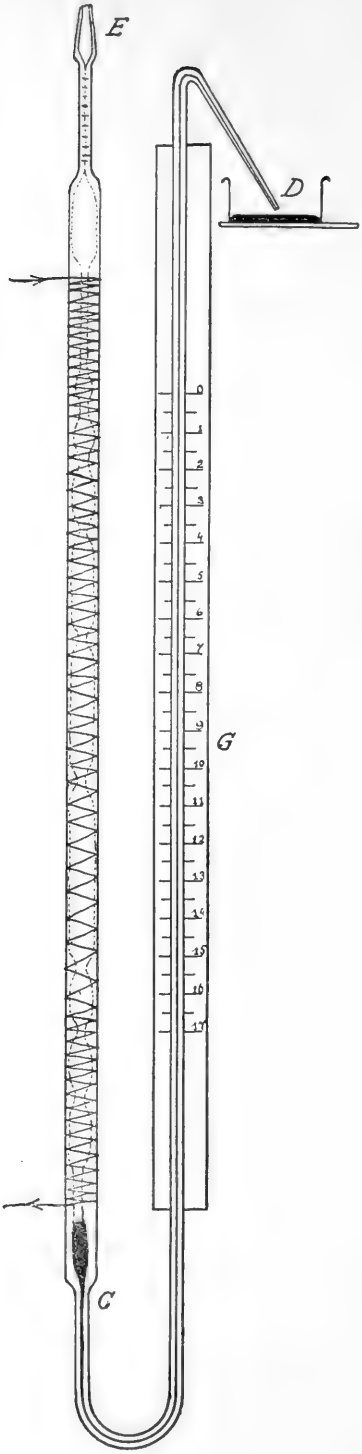

Fig. 5.

10 Ohms, is short-circuited, and so on at every following contact.

If we place the whole of the platinum wire in a Wheatstone bridge, it is clear that when the gas is compressed, so when the mercury in the tube rises, the resistance will be subjected to abrupt changes. This is observed by replacing the galvanometer needle of the bridge at zero, whenever a part of the platinum resistance has been shunted out by the mercury. At the outset of the experiment, when the measuring tube is still entirely filled with gas, the resistance of the whole platinum wire, which we shall call the volume wire, is in the bridge. Whenever a reservoir has been filled with mercury, the part of the volume wire wrapped round that reservoir, is short circuited.

The resistances of the different parts of which the volume wire consists, are known by the gauging of the measuring tubes. We shall now proceed to a discussion of this gauging.

An exceedingly narrow capillary *CD* is sealed to the measuring tube. This capillary has the same length as the measuring tube and is bent somewhat further round. The measuring tube is still open at the top, and has a prolongation *E*, to which a rubber tube can be fastened. An accurate scale-division *G* is attached to the narrow capillary. The capillary is drawn out thin at the top and bent.

If the end *D* is put in a vessel with mercury, the tubes will be filled with mercury, when the air is sucked off at *E*. When the mercury in the measuring tube is close to a point of contact, the mercury can be made to move to and fro past it by suction or pressure with two pumps[1] connected with *E* by means of a three-way cock. The volume wire is then again inserted into a WHEATSTONE bridge. The galvanometer needle deviates whenever the place of contact is passed. At the same time the mercury in the narrow capillary tube passes up and down along the scale. After some practice it is not difficult to read the position of the mercury in the latter tube at the moment that the galvanometer needle deviates. The best way to do this is of course when the mercury in the measuring tube rises, because the meniscus has then the same position as during the measurements.

If this has been done at a place of contact, the mercury may be pressed from the reservoir under it by increase of pressure of *E*, and the quantity that flows out at *D* may be received in a weighing bottle; then the level of the mercury in the capillary tube is again observed at the moment that the galvanometer deviates. It is clear

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[1] Two cycle pumps, in one of which the leather valve has been put reversed.

that in the meantime the resistance has changed, and the resistance in the resistance box must also be changed.

It is simple to determine the volume that was occupied by the mercury between the two places of contact. Let G be the weight of the expelled mercury, S_1 and S_2 the scalar heights which have been read, and f the weight of one scalar division of mercury, then $\{G + (S_1 - S_2)f\} : \Delta$ is equal to the required volume. (Δ is the specific weight at the temperature used). In this way the great advantage is reached that in the measurement any cocks and other movable parts are avoided.

Thus the different reservoirs are calibrated. The upmost reservoir is in an exceptional case. First of all there is no place of contact in it. It would not be practicable to make one there. Besides, to clean the tube after contamination the upmost point must be knocked off. In order to enable us yet to accurately know the volume of the upmost reservoir every time, the tube is drawn out very thin at the top. On this narrow part lines are etched at some millimeters' distance. When the tube is quite filled with mercury, the positions of the mercury at the etched lines can every time be compared with the position of the mercury along the scale. Thus the volumes can be expressed and calculated from line to line in scalar divisions, and also those from one of these lines to the upmost contact, after a quantity of mercury has been expelled.

To determine the weight of a scalar division of mercury, we make use of one of the places of contact. When the deviation of the galvanometer needle has been compared with the level of the mercury along the scale, we press out a drop of mercury, and again compare the mercury level with the same place of contact. The decrease of height agrees with the expelled drop of mercury, which is weighed, and then the scale is at least partially gauged. This can be done for different parts of the scale. Care can further be taken always to work within a certain, pretty small part of the scale. And the tube being very narrow, the differences of position are only to be taken into account as a correction.

During the measurements the whole tube is of course placed in a thermostat. On account of the length of the tube the thermostat is thus constructed. A glass tube of ± 6 cm. diameter passes at the bottom into a narrower tube, which is connected by a rubber tube with a large copper mixing vessel, where the water is kept at the desired temperature by means of a toluol-thermoregulator, stirrer, and burner. The glass tube is placed so high with respect to the liquid level in the mixing vessel that the measuring tube which is to be gauged, is quite immersed in the water; only the bent point *D*, in which there is no mercury during the measurements, projects above the water. By means of a water-jet air pump the water from the glass tube is sucked up, and conveyed to the mixing vessel, in the same way as the mercury is sucked up and thrown over (by air being sucked up at the same time) in the well-known KAHLBAUM air pump. The water from the mixing vessel flows of its own accord to the thermostat through the connection at the bottom, which secures a strong water current. Thus the required accuracy, at the utmost 0°.1, is easily obtained. Eventual variations in temperature can be taken into account, when the weight of the total quantity of mercury in the two tubes is known. This quantity is every time determined by pressing the remaining mercury from the tubes and weighing it when the last reservoir has been gauged. As a rule the temperature variations were not worth mentioning, and it was not necessary to apply temperature corrections.

When a measuring tube must be cleaned on account of contaminations, a piece may every time be knocked off at the top. After the cleaning the tube is fused to at the next line. This can be done so accurately, and the capillary is so narrow here, that it may be assumed that the volume of the tube is diminished by the known volume between the lines.

It is unnecessary to apply more than ten lines. After so many cleanings, the volume wire is damaged as a rule, if the tube was not broken before, and to repair the volume wire is very difficult. A newly wrapped tube is, indeed, always rubbed with zapon lac, but in the long run this measure is no safeguard for the thin volume wire.

That in this way an exceedingly accurate calibration is obtained, may appear from the following example. The values give the total volumes from the upper end of the tube to the different places of contact at two different calibrations.

7.0561	7.0554	20.0667	20.0590
7.4276	7.4281	25.0062	25.0078
8.0137	8.0121	34.5016	34.5005
8.8849	8.8843	43.7536	43.7516
11.5623	11.5595	85.4267	85.4287
14.9740	14.9709	87.5029	87.5008
		90.3264	90.3269

The differences are at most $^1/_{1000}$ of the values themselves, mostly however much smaller, and for the large volumes they are even of the order of 1 to 100.000. The mean error may safely be put at no more than one to 10.000, an accuracy which is certainly not reached for other sources of error in these measurements. Of course the values directly give only the volumes at the temperature and the pressure of the gauging. For other temperatures and pressures corrections must be applied, which we shall discuss in one of the following papers.

Amsterdam. *Physical Laboratory of the University.*

Geology. — "*Elephas antiquus Falc. from the river Waal near Nijmegen.*" By Dr. L. Rutten. (Communicated by Prof. Dr. A. Wichmann).

The dredging-works in the river Waal in the neighbourhood of Nijmegen have brought to light already many a finding of diluvial mammals.

By much the greater part of the bones found belong — as indeed nearly all remains of mammals dredged from our rivers — either to animals of the mammoth fauna[1]) or to animals of the postglacial fauna.

An exception to this rule is the fragment of a molar of *Elephas meridionalis* from the river Waal near Nijmegen,[2]) and this finding proved that in the sub-soil of the neighbourhood of Nijmegen also pliocene deposits must be found.

Mr. G. M. Kam of Nijmegen, who collects with laudable ardour all remains of mammals that are found in the neighbourhood of this town, showed me a short time ago a number of newly found typical molars of *Elephas primigenius Blum.* and moreover a molar belonging doubtlessly to *El. antiquus Falc.*, and which had been dredged from the river Waal, as were likewise the mammoth teeth.

Though the great stratigraphical value formerly ascribed to *Elephas antiquus*, has somewhat depreciated, because it is supposed from later discoveries that the *antiquus*-fauna and the *primigenius*-fauna, differ more facially than stratigraphically from each other,[3]) it seems however that, for our country, the rare fossils that are known of the *antiquus*-fauna are older than the remains of the *primigenius*-fauna.

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[1]) L. Rutten. Die diluvialen Säugetiere der Niederlande. Diss. Utrecht, 1909.

[2]) L. Rutten. Ibid., p. 15—16.

[3]) A.o. W. Soergel. Elephas trogontherii Pohl. und Elephas antiquus Falc. Palaeontographica. LX. 1912.

The newly found molar is most likely a third genuine molar of the left lower-jaw. It is much worn out by mastication, so that at the frontal side a few lamillas have already disappeared. Extant are still — $^1/_2$ 12x at 221 × 68 × 117 mm. During the wearing-out mastication there are formed on each lamina first a median, tape-shaped and two lateral, ring-shaped figures, which remain a long time separated, but finally fuse into a distinctly rhombic figure, so that the mastication-figures of two succeeding lamellas touch each other in the middle. (fig. 1). The enamel is $2^1/_2$—3 mm. thick and strongly plaited. The mentioned dimensions and characteristics are all extremely typical for *Elephas antiquus Falc.*

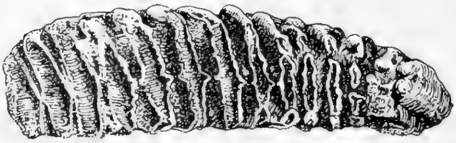

Fig. 1.

The molar was not much worn out and between the laminas it contained still a little ferruginous quartz-sand and some small pebbels of quartzite.

Much less typical is the remnant of mastication of another molar, belonging likewise most likely to *El. antiquus.* (fig. 2).

It contains still 4 laminae of 55 × 56 mm. and is most likely a fragment of a first genuine molar of the upper-jaw. The very strongly plaited enamel is $2—2^1/_2$ mm. thick. The figures of mastication can hardly be called rhombic; we must however take into consideration that these figures lose their typical character in the same measure as a molar is worn out by mastication. This fossil cannot possibly belong to *El. primigenius*; on account of its narrowness the molar shows the greatest affinity with *El. atiquus.*

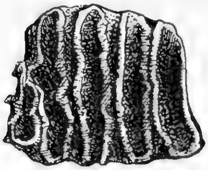

Fig. 2.

Chemistry. — *"On the nitration of methylurea."* By Dr. H. J. Backer. (Communicated by Prof. Franchimont).

The behaviour of methylurea and of ethylurea on nitration is considered as a remarkable instance of the different influence which the methyl and ethyl group can exert on the properties of a compound.[1]

Degner and von Pechmann [2]) have stated that with *methylurea* the nitration takes place at the *imino*-nitrogen atom, whereas according

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[1] Degner and von Pechmann, B. **30**, 654 (1897). Also compare V. Meyer and Jacobson's Lehrb. d. Org. Chemie I^2, 1394 (1913).

[2] B. **30**, 652 (1897).

to THIELE and LACHMAN [1]) *ethylurea* is nitrated at the *amino*-nitrogen atom. The nitration products thus should be :

a, a-methylnitro-urea, CH_3-N(NO_2)-CO-NH_2,
a, b-aethylnitro-urea, C_2H_5-NH-CO-NH-NO_2.

It has now been found that the idea as to the nitration of methylurea is not correct.

D. and v. P. carried out the reaction by treating the sulphuric acid solution of methylurea at a low temperature with the theoretical quantity of ethyl nitrate. As products, they obtained methylnitramine and a methylnitro-urea melting with decomposition at 156—157°.

I have carried out the nitration in various ways, namely with the theoretical quantity of ethyl nitrate or absolute nitric acid in sulphuric acid solution, and also by introducing the nitric acid compound of methylurea into sulphuric acid. Invariably, a compound was obtained decomposing between 90 and 100° with evolution of gas and having the composition of methylnitro-urea; methylnitramine was not formed.

If this product is dissolved in cold aqueous ammonia and then mixed with dilute sulphuric acid, methylnitro-urea is precipitated, melting with decomposition against 159°.

D. and v. P. state that this compound is decomposed by ammonia at 100° and then yields methylnitramine ; from this they conclude that it consists of *a, a*-methylnitro-urea.

It has now appeared, however, that this compound m.p. 159° is the *a, b*-methylnitro-urea ; I have proved this structure firstly by reduction to the corresponding semicarbazide and further by studying the behaviour towards different bases.

a. Reduction. This was carried out electrochemically, because also in the non-substituted urea the electrical reduction gives far better results than the chemical one [2]). The operation took place in dilute sulphuric acid with a cathode of tinned copper gauze.

The generated product with benzaldehyde gave a semicarbazone m.p. 166°. From the latter was formed, on heating with dilute sulphuric acid, the free methylsemicarbazide m.p. 118°. This compound when decomposed by alkalis gave the non-substituted hydrazine N_2H_4, and, hence, cannot be anything else but the hydrazinoformicmethylamide NH_2-NH-CO-NH-CH_3. Consequently the nitrocompound was the *a, b*-methyl-nitro-urea NH(NO_2)-CO-NH-CH_3.

In order to further confirm this conclusion the methylsemicarbazide

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[1]) A. **288**, 285 (1895).

[2]) R. **31**, 25 (1912).

was also prepared synthetically from methyl*iso*cyanate and hydrazine:

$$NH_2\text{-}NH_2 + CO : N\text{-}CH_3 = NH_2\text{-}NH\text{-}CO\text{-}NH\text{-}CH_3.$$

The product m.p. 118° proved to be identical with the methylsemicarbazide obtained by reduction. The above-mentioned condensation product with benzaldehyde (m.p. 166°) and the semicarbazones formed with other aldehydes were also identical.

b. Decomposition by bases. The reaction with bases affords a suitable means of deciding whether we are dealing with a primary nitramine or with an alkylnitramide. A primary nitramide $Ac\text{-}NH\text{-}NO_2$ will, on hydrolysis, yield nitramide NH_2NO_2, from which is formed on subsequent decomposition nitrous oxide N_2O, but an alkylnitramide $Ac\text{-}N(NO_2)R$ gives the monoalkylnitramine $RNHNO_2$.

Hence, the reaction of the *a,a*- and the *a,b*-methylnitro-urea will be expressed by the following equations:

$$a,a —. CH_3\text{-}N(NO_2)\text{-}CO\text{-}NH_2 + 3KOH =$$
$$= CH_3\text{-}N\text{-}NO_2K + K_2CO_3 + NH_3 + H_2O. \quad . \; . \; . \; . \quad (I)$$

$$a,b —. CH_3\text{-}NH\text{-}CO\text{-}NHNO_2 + 2\,KOH =$$
$$= CH_3\text{-}NH_2 + K_2CO_3 + N_2O + H_2O. \quad . \; . \; . \; . \quad (II)$$

The methylnitro-urea m.p. 159° on heating with bases gives one mol. of nitrous oxide; in addition methylamine is formed but no methylnitramine. These observations all agree with equation II, but they all are opposed to equation I.

The reaction of primary nitramides and alkylnitramides with ammonia differs somewhat from that with alkalis, but is still quite as useful for distinguishing the two classes. The decomposition of the two isomers by ammonia is represented by the following equations:

$$a,a — . CH_3\text{-}N(NO_2)\text{-}CO\text{-}NH_2 + 2\,NH_3 =$$
$$= CH_3\text{-}N\text{-}NO_2NH_4 + NH_2\text{-}CO\text{-}NH_2 \quad . \; . \quad (III)$$

$$a,b — . CH_3\text{-}NH\text{-}CO\text{-}NH\text{-}NO_2 + NH_3 =$$
$$= CH_3\text{-}NH\text{-}CO\text{-}NH_2 + N_2O + H_2O \quad . \; . \quad (IV)$$

The compound m.p. 159° gives on decomposition by ammonia methylurea (identified in the form of its nitroso-derivative) and no methylnitramine is formed. This tallies with equation IV, but not with equation III.

The reactions with alkalis and ammonia therefore prove that the methylnitro-urea m.p. 159° is, indeed, the *a,b*-compound.

Further, I have investigated the crude nitration product before it was treated with ammonia.

This product which melts very unsharply (at about 90°—100°)

with evolution of gas, has the empirical composition of methylnitro-urea and yet on purifying with ammonia, we obtain only about half the weight of *a,b*-methylnitro-urea. Hence the presumption that the admixture consists of the isomere, *a,a*-methylnitro-urea.

As a matter of fact, on treating this crude product with alkalis or ammonia, methylnitramine is formed which I was able to show by the melting point and other properties. On decomposing with baryta water a quantity of methylnitramine was obtained, pointing to the presence of 40°/₀ *a, a*-methylnitro-urea.

The quantity of nitrous oxide formed on heating with potassium hydroxide indicated 55°/₀ of *a,b*-compound in the mixture.

Summary of the results.

1. On nitrating methylurea in sulphuric acid solution a mixture is formed of the two isomeric mononitro-derivatives.

2. On treating this mixture with cold ammonia solution, the *a, a*-methylnitro-urea is decomposed, whilst the *a, b*-compound is converted into its ammonium salt and is obtained in a pure condition by addition of an acid.

The structure of this *a, b*-methylnitro-urea is proved:

a. by reduction: hydrazino-formic-methylamide NH_2-NH-CO-NH-CH_3 is formed, the composition of which is proved analytically (formation of hydrazine on heating with alkalis) and synthetically (preparation from N_2H_4 and $CONCH_3$).

b. by the decomposition with alkalis and ammonia, which agrees in all respects with the formula of the *a, b*-compound and is opposed to the formula of the *a, a*-compound.

3. The mixture of the isomers found in one of the nitration experiments contained about 55 °/₀ of the *a, b*-methylnitro-urea and, as appears from the decomposition with bases, fully 40 °/₀ of the *a, a*-compound.

4. The essential difference in the behaviour of methylurea and ethylurea towards nitration agents, as accepted up to the present, is herewith annulled.

The experimental details and the new compounds obtained in this study will be described elsewhere.

Botany. — *"The primary photo-growthreaction and the cause of the positive phototropism in Phycomyces nitens."* By Dr. A. H. Blaauw. (Communicated by Prof. F. A. F. C. Went.)

(Communicated in the meeting of December 27, 1913).

There are numerous investigations of the curvature movements, which plants execute, when energy is supplied unilaterally in the form of light or warmth, or when the organs of plants are displaced from the position, which they naturally occupy with respect to gravity.

The investigation of these "tropistic" movements, has proceeded especially in recent years with greater precision, after it was found in 1908, that for the understanding of these curvature-phenomena it is necessary to observe the effect *of definite quantities of energy.* But whilst in this way more and more data have been collected, concerning the curving of organs as a result of a unilateral action of energy, there lagged behind all the more the study of the effect of energy, when applied to the organs not asymmetrically but radially. The occurrence of curvatures as a result of asymmetrical forces, is a phenomenon so striking, that it is easy to understand that much more attention has been paid to the study of curvatures than to phenomena, which occur when the quantities of energy are supplied radially symmetrically to the organs of the plant. Yet it is as a matter of fact more natural to investigate first the influence exercised on an organ by energy, such as light or warmth, when its action is distributed uniformly on all sides of that organ, and only afterwards to consider as a special case what happens, when the energy reaches the plant not equilaterally, but from one definite side.

Now since it is a very important and well-known phenomenon, that the plant reacts to this asymmetric energy in a striking manner controlled by fixed laws, it was hardly conceivable that the plant would not also react distinctly in the more general case in which the energy acts radially symmetrically. With this equilateral action a marked curvature was no longer to be expected, but it was possible that any reaction taking place might not be limited to certain chemical changes in the cells, difficult to demonstrate, but might express itself more clearly in a change in the rate of growth, which change might be susceptible of measurement.

After earlier investigations with light applied unilaterally, it seemed to me desirable in consequence of the above considerations to pass no further judgment as to the value and essence of curvature reactions, until a further inquiry had been made into the way in which a growing organ reacts when light, warmth or centrifugal force acts in definite quantity on that organ uniformly from all sides. The first results of such an inquiry with respect to light will now be described.

For various reasons I have chosen in the first place the sporangiophores of *Phycomyces* as objects for investigation. The most important of these reasons was, that it was obviously desirable first to trace the influence of light on a single cell and only then to investigate it in multicellular organs such as the stem and the root of higher plants.

I have postponed for later more detailed description an account of the arrangement for securing a constant temperature, of the method of cultivation and of other details. I will here only mention, that the fungus was grown at the same constant temperature at which the experiment was afterwards carried out. During the experiments the temperature remained constant within $^1/_{50}$° C. I found that a rapid rise of temperature of, for example, only $^1/_{10}$° C., may exercise a considerable influence on the rate of growth of the sporangiophores, if it be only for a few minutes.

It can be noticed, that with the small, but sudden rise of $^1/_{10}$° C. the rate of growth may for a short time decrease by as much as 25°/$_0$, and then only rise again to the normal. In this case it is perhaps not the temperature itself, which directly affects growth, but a brief change in the degree of humidity of the atmosphere round the plant. I hope to deal with this more in detail. The chief point here is to show, how important it is to attain a high degree of constancy in experiments of this nature.

In the experiments sporangiophores are used, which are three to four cm. high. It is known from ERRERA's investigation (*Bot. Zeitung* 42^{ei} *Jahrg.* 1884) that they are then in a condition, in which they possess a maximal and practically constant growth.

The sporangiophore employed, is placed in the centre of a box, which remains therefore at a very constant temperature and in which the atmosphere has a rather high degree of humidity, which throughout the experiment remains quite constant. The growth is observed through a double plate of thick glass, by means of a telescope placed outside the box and magnifying 40 times. The light for the observation was obtained from a weak, red lamp, which was switched on only during the observation, for as short a time as possible; its feeble light, also passing through a double glass plate, forms a silhouette of the plant on a red background. The illumination of the plant, placed in a central position, is carried out by allowing light to fall from above through a double plate of glass. Whilst the plant is prevented from being illuminated directly from above, the light first falls on 8 little mirrors, which are arranged in a circle at equal distances round the central sporangiophore at an angle of 45° with respect to the incident rays. In this way the sporangiophore receives radially symmetrically the same illumination on 8 sides. For various reasons — to be later dealt with in greater detail — this arrangement was the more satisfactory.

The growth of the sporangiophore is always determined before illumination by several observations at intervals of 5 to 10 min. Whilst the variation in growth of different sporangiophores is considerable, the growth of any individual one in successive minutes is very uniform, especially when it is remembered with regard to the figures found, that with observations at short intervals the error of observation may be fairly large, because with weak, red light the measurement must always be made fairly rapidly. The figures of growth in the dark agree very well with those of ERRERA. In the first series of experiments with 8-sided illumination at 22° C. figures were mostly found, which fell below the maximal growth according to ERRERA, in the later experiments with unilateral illumination at 18°.3 C., after the method of culture had been somewhat modified, a value was generally found which agreed with the values found by ERRERA during maximal growth. The eventual relative variations in the rate of growth caused by the influence of light were however more important than the absolute rate.

In the first experiments the plant was illuminated via the mirrors on *each* of the 8 sides with 14 metre candle power during 15 sec., that is, eight times the quantity, which, given by one mirror only, would have effected a decided curvature. When a growing cell receives this amount of illumination, a very striking reaction of the growth takes place. This reaction is all the more marked, the closer the observations after illumination follow each other; for this reason observations were made as far as possible every two minutes after illumination. We then notice:

1. that immediately after illumination growth still remains the same for about 3 min.

2. that after about 3 min. growth at once markedly increases to reach a maximum $4^1/_2$ to 8 min. after illumination; with this quantity of light the maximum is usually not less than 2 or 3 times the normal rate of growth.

3. that afterwards the rate of growth again diminishes to its normal value which is reached about 7—16 min. after illumination.

4. that often however the rate sinks to 10 to 30°/₀ below its

normal value for some minutes, and then later becomes quite normal again.

This is a short résumé of the reaction, which these growing cells execute after illumination by the above-mentioned definite quantity of light and there was among the dozens of cells, which I investigated in this manner not a single one which did not clearly show this remarkably strong reaction. Moreover the phenomenon equally occurred both in slow-growing and in rapidly growing cells.

Of this series of experiments, only a few examples will for the sake of brevity, be given in tables I, II, and III, of which the third is also represented graphically in fig. 1. If observations are not made every two minutes but at long intervals, the reaction then does not appear to be so striking, whilst with observations made at still shorter intervals than two minutes, for a very short time perhaps a still higher figure for the maximum growth might be found, than has here been noted in observations taken every two minutes.

If the cell is illuminated with the same intensity of light for a 4 times shorter period, there likewise always occurs a distinct acceleration of growth, but the latter reaches a somewhat lower value, about $1^1/_2$ to 2 times the normal; if the illumination is 4 times as strong and 4 times as long, that is to say 16 times as great, then growth increases not nearly so much as with the lesser illumination and reaches a value of $1^1/_3$ to $1^1/_2$ times the normal.

Whilst these experiments are being continued in greater detail and more accurately in order to determine on the one hand, with how small a quantity of light a measurable reaction still occurs and to trace, on the other hand, what happens further after giving a much greater quantity of light, my immediate purpose is to report the fact, that the growth of the cells responds with a sharply accentuated reaction to illumination with a certain quantity of light, a reaction which shows the typical character of what hitherto has been called in botanical literature a stimulus-reaction. This reaction of growth to light I should like to name *photo-growth-reaction*, but considering, that many as yet unanalysed phenomena in which light has an influence on growth or form, may also be included under this general name, I will in order to prevent confusion, distinguish this reaction as *primary photo-growth-reaction*. In the case of an accelaration of growth we can then speak of a positive, in the case of retardation of a negative photo-growth-reaction.

With regard to the existence of a sharply-defined reaction of this kind, practically nothing can be deduced from the literature-references, at least the general opinion about the influence of light on growth

TABLE I.

At 2.38¾ p. m. illuminated on 8 sides with 14 metre-candle power for 15 sec.

Time of observation	Position of the Sporangium. one scale division = 49μ	Increase in length per minute in scale-divisions
2.32½	48½	0.88
2.40½	55¼	0.88
2.42½	57	2.00
2.44½	61	2.25
2.46½	65½	1.00
2.48½	67½	0.75
2.50½	69	

TABLE II.

At 4.32 p. m. illuminated with ± 14 metre-candle power for 15 sec. on 8 sides.

Time of observation	Position of the Sporangium. one scale division = 49μ	Increase in length per minute in scale-division
4.15	25	0.87
4.22½	31½	0.88
4.31	39	1.00
4.33	41	0.80
4.35½	43	1.83
4.37	45¾	1.50
4.38½	48	1.33
4.40	50	1.00
4.41½	51½	0.67
4.43	52½	0.58
4.46	54¼	0.55
4.51	57½	0.81
4.55	60¾	

TABLE III.

A specimen of weak growth illuminated at 2.52 p. m. with 14 metre-candle-power for 15 sec. on 8 sides.

Time of observation.	Position of the Sporangium one scale division = 49μ	Increase in length per minute in scale division.
2.39½	39	0.36
2.50½	43	
2.52	Illumination	0.33
2.53½	44	0.40
2.56	45	0.50
2.58	46	0.75
3 p. m.	47½	0.75
3. 2	49	0.50
3. 4	50	0.50
3. 7	51½	0.35
3.12	53¼	0.38
3.22	57	

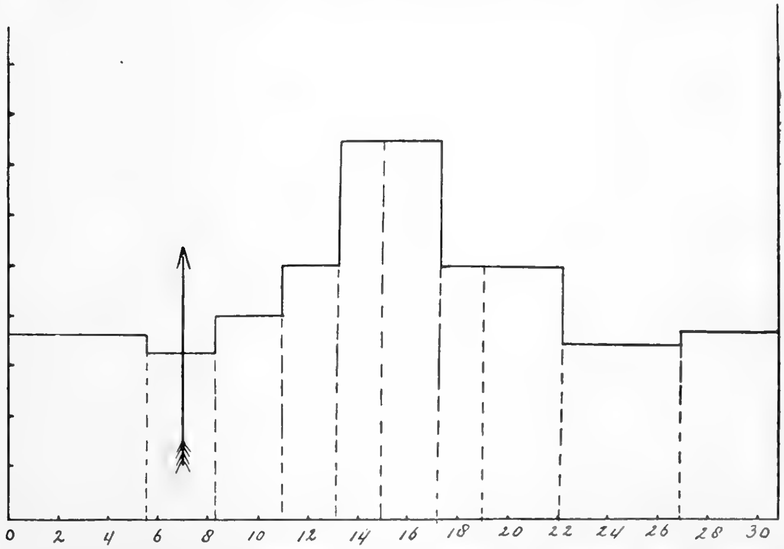


Fig. 1. Graphical representation of a case of positive photo-growth-reaction (Table III). The arrow gives the moment at which there was illumination for 15 sec. with 14 metre-candle-power, on 8 sides. The abscissa gives the time in minutes, the ordinate the ratio of the rates of growth.

is completely at variance with these facts. In the first place so far as concerns the positive or negative influence of light. The general conception, supported by numerous facts, is that light in general exercises a retarding influence on growth. In PFEFFER's *Pflanzenphysiologie* (2e *Aufl.* 1904, *Bd.* II. *blz.* 108) as a result of facts then known this conception is thus formulated: "Innerhalb der zulässigen Lichtgrenzen wird, so weit bekannt, in der phototonischen Pflanze durch Verminderung der Beleuchtung eine gewisse Beschleuniging, durch Zunahme der Helligkeit eine gewisse Verlangsamung der Zuwachsbewegung bewirkt".

In particular this was also deduced from the experiments of VINES (*Arb. Würzburg II,* 1878), who observed the growth of the sporangiophores of *Phycomyces* every hour or half hour in daylight and in the dark and found a slightly smaller growth in the light period than in the dark. In this investigation, as in that of others, too large and too indefinite quantities of light were used; moreover most investigators, including VINES, used intermittent stimulation, for which reason the influence of illumination made itself felt as an after effect also in the dark periods and conversely. Further in VINES' experiments the temperature is very variable, in some it changed for example from $22^1/_2$° C.—26° C.

Whilst nearly all earlier investigators found a smaller growth in the light than in the dark, HELENE JACOBI (*Sitzungsber. d. K. Ak. d. W. z. Wien, Abt. I, Bd.* 120, 1911) made the statement that, for example, plants of *Triticum* and *Phaseolus,* which had been illuminated 24 hours before for a fairly short time, had become slightly larger, than the non-illuminated controls. In this investigation, however, the growth was not measured until 24 hours later and then only with the naked eye, whilst the humidity and the temperature varied very greatly during many experiments. In comparison with this VINES' investigation of 1878 may almost be called modern, for he worked with a telescope, ensured a fairly constant humidity and did not wait for 24 hours before taking his readings.

Further more the representation in the literature of the nature of the growth reaction induced by light is at variance with the above facts. The current conception of this nature is summarised by PFEFFER as follows (blz. 109): "Selbst bei dem Uebergang von einer hellen Beleuchtung zu voller Finsterniss, oder umgekehrt, wird die Wachsthumsschnelligkeit gewöhnlich nur um 5—30 %, selten um 50 % oder mehr beschleunigt, resp. verlangsamt, und bei schwächerem Beleuchtungswechsel lässt sich eine Reaktion nicht immer nachweisen". PFEFFER further indicates, that a change in the rate of growth does not occur rapidly but gradually, and concludes: "Neben dieser allmählichen Verschiebung der Wachsthumsschnelligkeit scheint durch einen plötzlichen Beleuchtungswechsel der Regel nach keine auffällige transitorische Reaktion veranlasst zu werden".

These conceptions, which contrast with the photo-growth-reaction now demonstrated in *Phycomyces*, are caused by various facts: that very large quantities of light were used, which greatly exceeded the optimum; that the illumination was very prolonged, so that the plant partly adjusted itself again to the light; that the illumination was frequently intermittent, so that the phenomenon was not analysed, but became more complex; and because observations were made at too great intervals, so that the values for a possibly accentuated reaction were lost in a more average value.

TABLE IV.

From 1.1½ p.m. to 1.2½ p.m. unilateral.

Illumination with 14 metre candle power for 60 sec.

Time of observation.	Position of the sporangium.	Increase in length per minutes in scale divisions	Remarks.
1.37½ p.m.	40	1.07	
1.51½	55	1.00	
1.58½	62		
2. 1½—2½	Illumination	0.85	
2. 5½	68	2.00	
2. 7	71	2.00	
2. 9	75	1.20	
2.11½	78	1.25	
2.13½	80½	[0.88]*)	Begin. of pos. curvature.
2.15½	[82¼]	[0.88]	Increasing curvature.
2.17½	[84]	[0.75]	" "
2.19½	[85½]		

*) From this time onwards the amount of growth is uncertain on account of the occurrence of the curvature.

After the completion of these experiments with *Phycomyces* I hope to study the behaviour of the stem and the root in higher plants.

After the phenomenon described above had been established qualitatively, I was naturally curious as to how far this photo-growth-reaction was related to the well-known phototropism of *Phycomyces.* In order to investigate this, the plant was illuminated unilaterally with, for example, 14 metre candle power during 60 sec. and at the same time the growth and the occurrence of a curvature were watched through a telescope.

It was then found that — excluding the special case, which is described below — *a positive curvature never appears, unless the above-described acceleration of growth has previously taken place.* The positive photo-growth-reaction occurs in the usual manner after about 3 min. — this time of reaction can with the weakest illuminations rise to 7 min. — it reaches its maximum, then the rate of growth diminishes again, and from this moment does the positive phototropic curvature become visible, which, according to the conditions of illumination becomes more or less strong. A few examples are given in tables IV and V.

TABLE V.

From 3.41 to 3.42 p.m. unilateral illumination with 14 metre candle power for 60 sec.

Time of observation	Position of the Sporangium.	Increase in length per minute in scale divisions	Remarks
3.25½ p.m.	30	1.00	
3.33	37½	0.95	
3.41 3.42	Illumination		
3.43	47	1.13	
3.45	49¼	1.50	
3.47	52¼	1.50	
3.49	55¼	[1.00]	Beginning of curvature
3.51	[57¼]	[0.88]	Obvious curvature
3.53	[59]	[1.00]	Increasing curvature
3.55	[61]		„ „

When one considers that the rays, which practically run parallel, fall on the sporangiophores, as on a cylindrical lens, then the course of the rays in the body of the cell can be conceived as in fig. 2. It will be seen that the illumination of the front and of the back of the cell necessarily must differ rather widely. There passes indeed as much light through the front-*half* as through the back *half*, but by far the greater part of the posterior wall the peripheral protoplasm is more strongly illuminated than that of the anterior wall; in the middle of the posterior wall about twice as strongly as in the middle of the anterior wall. With illumination which is neither too strong nor too weak, the photo-growth reaction of both sides commences at the same moment after about 3 min., but this acceleration of growth continues at the end of the reaction somewhat longer at the back than at the front and consequently after the cell has shown a certain acceleration of growth, a curvature arises by the action from that side, which is most strongly illuminated.

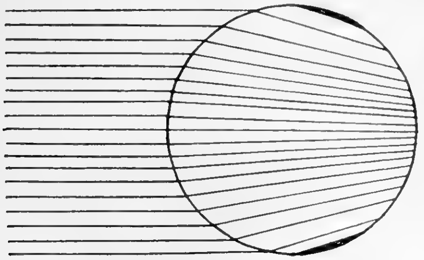


Fig. 2.

The experiments concerning the absence of positive curvature and occurrence of a negative one with large quantities of light, will be continued in connection with results, to be obtained with the photo-growth-reaction after omnilateral strong illumination. But in my opinion the explanation of the positive phototropism in *Phycomyces* has already been given by the above, and moreover I found in the following facts new supports for this conclusion.

I subsequently investigated what happens, when the unilateral illumination is made weaker so that the lower limit of phototropism is approached. We may now expect, according to the course of the rays (see fig. 2) that a quantity of light would finally be reached, which is too small to effect an increased stretching of the cell-wall on the anterior side, but in consequence of refraction is just sufficient to cause acceleration of growth on the posterior side. And that is indeed what is found! Table VI gives an example of the different cases of this kind which I observed.

In this way acceleration of growth was no longer observed; at the moment at which it would otherwise occur — that is after a reaction-time of 5—7 min. with this very weak illumination — the growth of the most strongly illuminated part of the cell-wall only is accelerated and the only result is a curvature, which is weak and often disappears again after a few minutes.

TABLE VI.

At 3.40 p.m. unilateral illumination with about 2$^{1}/_{2}$ metre-candle for 4 sec.

Time of observation	Position of the Sporangium	Increase in length per minute in scale divisions	Remarks
3.18$^{3}/_{4}$ p.m.	30		
		0.92	
3.30$^{3}/_{4}$	41		
		0.96	
3.37	47		
3.40	Illumination	1.00	
3.41	51		
		1.00	
3.43	53		
		0.88	
3.45$^{1}/_{4}$	55		
		1.00	
3.47$^{1}/_{4}$	57		Beginning of curvature
		1.00	
3.49$^{1}/_{4}$	59		Increasing curvature
		1.00	
3.51$^{1}/_{4}$	61		Curvature stops
		0.90	
3.56$^{1}/_{4}$	65$^{1}/_{2}$		Curvature goes back

The curvature is thus seen to occur with a very small quantity of light (2$^{1}/_{2}$ to 10 metre-candle-seconds) and these curvatures, which already appear after 5—7 min. and are mostly weak, have not been noticed by me before. Formerly I found a curvature only with the most sensitive specimens, for example, after 50 metre-candle-seconds. That was the curvature discussed above which occurs, when the acceleration of growth has already passed off and of which the reaction-time (observations being made with a telescope) amounts to 8—15 min. at least. We see therefore, that as a necessary result of the photo-growth-reaction and the refraction of light, weaker curvatures also occur with still less illumination and these of necessity have a rather shorter reaction-time.

Whilst then these small curvatures are visible with 2$^{1}/_{2}$ to 10 Metre-candle-seconds in proof of a liminal local acceleration of the stretching of the cell wall, there occurs with a slightly stronger illumination or with the same illumination in "more sensitive" specimens — a reaction, which also could have been anticipated. In such cases, as those of table VII the quantity of light is just sufficient to cause a slight acceleration of growth in the anterior wall. Since the posterior side is somewhat more strongly illuminated than the anterior one, which only just reacts, the posterior side therefore begins to react sooner: after 4 to 5 min. a very slight curvature occurs, after about 7 min. the anterior wall also reacts, the very slight curvature does not continue or may even disappear, but a distinct acceleration of growth of the entire cell can be observed and as this passes off, there again occurs also a very slight curvature, since the rather more strongly illuminated posterior wall not only begins to react earlier, but continues to react somewhat longer than the anterior wall, which falls just within the reach of a growth acceleration. The phototropic curvature is thus divided here into two and both parts remain very slight. If somewhat more light is supplied, the reaction-times of the anterior and the posterior-wall

TABLE VII.

At 4.1½ p.m. unilateral illumination with about 2½ metre candle power for 5 sec.

Time of observations	Position of the sporangium	Increase in length per minute in scale-divisions	Remarks
3.42	47½		
		0.97	
3.49¼	54½		
		0.96	
3.55	60		
4. 1½	Illumination	1.00	
4. 2½	67½		
		1.00	
4. 4½	69½		
		1.00	
4. 6½	71½		Beginning of curvature
		1.25	
4. 8½	74		Curvature slightly greater
		1.63	
4.10½	77¼		Curvature no greater
		1.50	
4.12½	80¼		Curvature back
		1.10	
4.15	83		
		0.80	
4.17½	85		Curvature again
		0.75	
4.19½	86½		Very feeble curvature
		0.83	
4.22½	89		Curvature no greater

become very much the same and the curvature — and that is the definitive phototropic curvature of *Phycomyces* — only appears after the maximum of the acceleration of growth, because the growth-reaction of the less illuminated anterior wall diminishes somewhat more rapidly than that of the posterior wall.

To be on the safe side I will not extend the scope of these facts further than to the positive phototropism of *Phycomyces,* but of this phenomenon I think, that proof has now been furnished, that *the appearance of these curvatures is the result of an asymmetrical modification of the growth of different sides of the cell, caused by the asymmetrical illumination of these sides*; *that for this case therefore* DE CANDOLLE'*s simple and ancient theory* — more particularly in contradiction to the later conception of SACHS — *is reestablished and with this a theory of a perception of the light-direction itself is superfluous.*

In the meantime I do not wish to generalize, but only to await the results of further investigations, which are being continued in various directions, on *Phycomyces* and on the root and stem of higher plants. Only, in my opinion, for no single one of these cases can any decisive proof in the literature be found against DE CANDOLLE's theory.

Finally I desire to express my great indebtedness for the facilities afforded me in the Laboratory of the TEYLER Foundation, for carrying out these experiments — and it is no mere formality, that I tender my thanks especially to the conservator, Jhr. Dr. G. ELIAS, for his assistance and interest in the arrangements for this investigation.

Haarlem, Dec. 1013.

Physics. — "*Magnetic researches.* X. *Apparatus for the general cryomagnetic investigation of substances of small susceptibility.*"

By H. KAMERLINGH ONNES and ALBERT PERRIER. Communication N°. 139*a* from the Physical Laboratory at Leiden. (Continued). (Communicated by Prof. H. KAMERLINGH ONNES.)

§ 7. *Sources of error. Sensibility. Accuracy. Disturbing magnetic influences.* The action of the magnet upon the carrier without the experimental tube appeared to be negligible, even when the lower end of the carrier was reduced to the temperature of liquid hydrogen. The action upon the coil of the carrier was also imperceptible even when a much stronger current i_m was passed through this coil than was used in our experiments[1]). Moreover, even if it should be of any importance, it would be eliminated by the above indicated method of observation. The influence of the stationary coil upon the higher conducting spring is probably not negligible, but it cannot cause any errors, as neither in the calibration nor in the observations is anything changed in this spring.

It may also be mentioned that by the manner in which the conductors are arranged, in connection with the order in which readings are taken, any influence of the electro-magnet or the rheostats upon the ammeters or of these upon each other, are eliminated. These influences are moreover very small.

Capillary action. At first we were rather uneasy about the capillary action between the rods of the floats and the mercury surface, and between the carriers of the experimental tube and the surface of the liquid in the bath. The regular return of the carriers to the same zero, proved that no disturbances from these causes occurred in our experiments. We had always given great care to keeping the mercury surface as pure as possible.

Vibrations. Vibrations of the ground have a very injurious effect upon the observations, as they are reproduced in the apparatus, greatly magnified, and are likely to cause troublesome swinging of the floating carrier. Vibrations in the microscope caused by the vibration of the ground, which troubled us at first, could be avoided by fixing the microscope more firmly.

The carrier is moved by every change of the forces that act upon it, which causes vertical oscillations of great amplitude. To damp these, glass wings are attached to the floats, so that after 2 or 3 swings they come to rest. Finally, the vapour bubbles that constantly rise in the bath, cause small vertical movements of the carrier, which are more marked, the greater the density of the liquid gas is. Against these vibrations the comparatively large inert mass — about 200 grams — of the carrier combined with the damping just mentioned, proved to be the best expedient. The damping could as a matter of fact have been made much greater, without any difficulty. But it was better not to go any further, as it would have made the movements of the apparatus aperiodic, and a few swings were very useful to bring the influence of the capillary action upon the carriers each time to the same value.

---

[1]) When the axis of the coil falls exactly in the plane of symmetry of the poles and goes through the middle of the interferrum this force is strictly zero.

Sources of error in the experimental objects themselves:

For the calculation of the specific magnetisation,we need to know the *mass per unit of length* of the substance with which the experimental tube is filled The total mass which the tube contains can be ascertained as accurately as we wish, but the length over which it is spread in the tube, owing to the irregularity of the extremities cannot be determined more accurately than within 0.2 to 0.3 m.m.

Further, it is assumed in the calculation that it is evenly distributed over the whole tube which cannot be strictly accurate, owing to slight differences in diameter and slight differences in the degree of closeness which is attained in filling to different heights, but this error is certainly small, and only influences the *absolute* value of the *calculated susceptibility;* if the same experimental tube is used in the same position at the various temperatures, this error has no effect upon the *relative* results, which are the principle object of our research.

The relative results may however become inaccurate, if between two experiments at different temperatures, some anisotropic grains, which together form an isotropic mass, each take a different direction, e. g. so that the line of greatest susceptibility in them approaches the direction of the lines of force, since the mean susceptibility of the group will thereby be changed. We can avoid that this happens unnoticed, by taking the observations at low temperature between two observations at ordinary temperature. To answer the more general question in how far an apparent isotropy can be obtained with substances which are in reality anisotropic, by pressing them in a more or less finely granulated condition into tubes of 5 to 8 m.m. we can, without changing the conditions in any other respect, repeat the experiments after having brought the experimental tube into another direction relatively to the lines of force, by turning it on its axis. In doubtful cases we applied this method.

Numerical data: The coils described, can carry currents of 6 amp. (i_f) and 1,5 amp. (i_m) respectively, for a quarter of an hour; the force which they then exert upon each other is about 25 grams. In the given arrangement this may therefore be regarded as the limit of the force which can be measured with the apparatus. Under favourable circumstances (little vibration) a change of 0,001 gram in the force acting upon the carrier can be observed. Generally speaking, the para-magnetic substances examined caused attractions of a few grams, sometimes even more. The accuracy of the results is therefore more limited by the accuracy of the ammeters, than by that of the apparatus itself. With two of the ammeters, in each of which we constantly adjusted on one of the scale divisions, it was possible to bring the relative sensibility to within a thousandth. The third was almost equally accurate. In the relative measurements of the susceptibility calculated, we can thus rely in general upon an accuracy of 0,2 to 0,3 %. The absolute accuracy suffers somewhat from the fact that we are not certain of the homogeneity of the experimental object (see above); but it is principally limited by the accuracy of the determination of the magnetic field, the square of which occurs in the formula for the susceptibility, and not by that of the apparatus.

There is one more important factor to be considered, viz. the constancy of the temperature of the bath. Disturbances in this will have a different effect with different substances, as the change in the susceptibility with the temperature is very unequal for different substances, especially when we approach the absolute zero.

In our experiments in general we did not observe any disturbances from irregularity of temperature. Only in the case of gadolinium sulphate, the susceptibility of which changes most with the temperature (1 % for 0,2 degrees at 20° K.) the measurements in different fields (at different moments therefore) did not agree so well with each other as might have been expected if we only considered the accuracy of the magnetic determinations.

(**February 26, 1914**).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday February 28, 1914.
Vol. XVI.

President: Prof. H. A. Lorentz.
Secretary: Prof. P. Zeeman.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 28 Februari 1914, Dl. XXII).

CONTENTS.

Mineralogy. — *"Röntgenpatterns of Boracite, obtained above and below its inversion-temperature".* By Prof. H. Haga and Prof. F. M. Jaeger.

(Communicated in the meeting of January 31, 1914).

§ **1.** Comparison of numerous photographic diffraction-patterns, obtained by the method of Laue, Knipping, and Friedrich, i.e. by the transmission of Röntgen-rays through planparallel crystalplates, has led with increasing evidence to the conviction, that the symmetry of those patterns agrees with that of the space-lattice, which presents itself as the very fundament of the molecular arrangement of the investigated crystal. On this assumption, the new method of research will be in future a very important manner to elucidate the question, if with polymorphic changes, and principally in cases of enantiotropic inversions in the neighbourhood of the critical inversion-temperature, a change of the molecular arrangement takes place, or if the cause of polymorphism must be attributed to a change only of the crystalmolecules themselves.

This problem seemed to us of high importance, especially in the case of those remarkable reversible inversions, which are found in a class of crystals, whose optical behaviour does *not* agree with the symmetry of their external form, of their cohesion, etc., or generally speaking: with their total crystallographic character; so that it has been a custom already from an early date, to discern these cases as those of "optically anomalous" crystals. Of this class of mimetic crystals the minerals *boracite*: $Mg_7 B_{16} O_{30} Cl_2$, and *leucite*: $K_2 Al_2 Si_4 O_{12}$ may, after the investigations of Mallard, Klein, etc., be considered to be typical representatives.

The boracite crystallizes in forms, which by no means can be discerned from real hexakistetraëdrical ones; even by the most accurate goniometrical measurements it appeared to be impossible to find any deviation of the external form from those possessing the above mentioned symmetry. On the other hand, however, the optical investigations, and also those concerning the corrosion-phenomena, have shown with perfect evidence, that the crystals of boracite possess *no* regular symmetry in the common way; they must be considered as composed by a very complicated system of birefringent lamellae, which according to their optical properties, cannot have any higher symmetry than that of rhombic crystals; these lamellae have intergrown in such a way, that their conglomerate corresponds, with respect to its external form, very exactly with a true regular crystal. More particularly the individuals of boracite seem to represent

H. HAGA and F. M. JAEGER. Röntgen-Patterns of Boracite below and above its inversion-temperature.

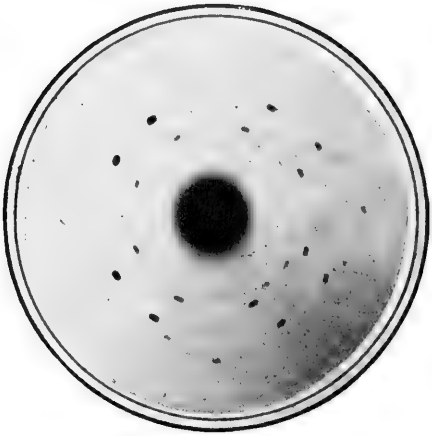


Fig 2.

Boracite 18° C. Distance: 42.5 mM.

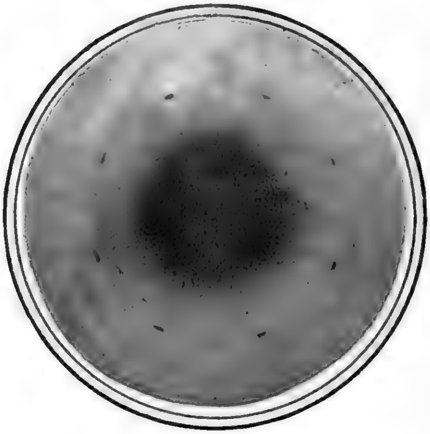


Fig. 3.

Boracite 300° C. Distance: 61 mM.

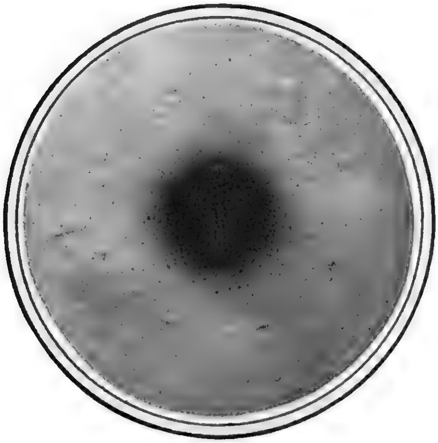


Fig. 4.

Boracite 18° C. Distance: 61 mM.

a polysynthetic twinformation of six hemimorphic rhombic crystals, whose twinning-planes are those of the apparent rhombendodecahedron. Normal to every plane of this form, the interference-image of a biaxial crystal can be observed in convergent polarised light, the plane of the optical axes being parallel to the longer diagonal of each face of the pseudo-rhombendodecahedron. At temperatures between 260° and 280° C., the boracite suddenly becomes optically isotropous; then it has got perfectly regular, and its optical properties are now in complete agreement with its external form. On cooling, the original birefringence returns as suddenly, as it has gone; the crystal represents afterwards again the case of an optically anomalous one.

These general considerations will be sufficient here for our purpose; therefore we will now begin the description of our experiments.

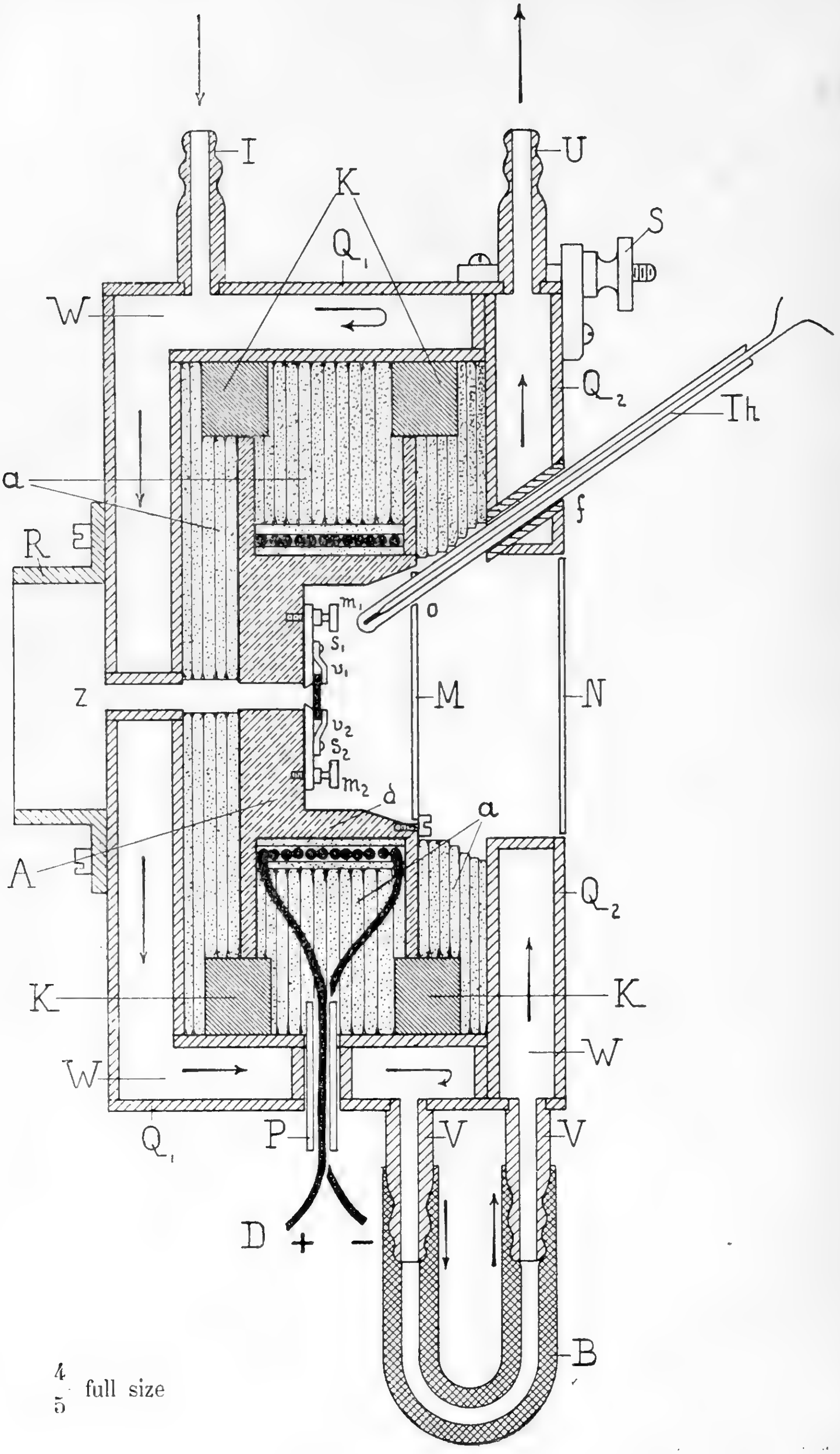
§ **2.** *The heating-apparatus.* To fulfil the condition, that the Röntgen-rays might be transmitted as well at higher as at lower temperatures, a furnace of the form described here in detail, was constructed.

A box with double walls was made of polished brass; it incloses the whole furnace like a screen, and is kept at a constant temperature by means of a circulating stream of cold water. The hollow box is composed of two separate parts: one of them Q_1 bears a tube R, which can be connected with the Röntgen-apparatus; further it has a cylindrical hole z, serving as a canal for the thin bundle of Röntgen-rays. Cold water enters the box at I; after circulation it goes by V and B to the hollow cover Q_2, and leaves the apparatus at U. The cover Q_2 is fixed in position on Q_1 by means of three equidistant screws S. Q_2 possesses at f an oblique perforation, which serves for the adjustment of the thermoelement Th.

The heating-coil D consists of platinum-wire, 0,4 m.m. in diameter; it enters the furnace at P, where it is insulated from the brass box by means of a porcelain-tube, and leaves the apparatus in the same way by a second hole of this kind. The heating coil is wound round a core of copper A[1]), from which it is insulated by means of a thin layer of asbestos-paper; the coil needs to be applied only in a single layer. The metal core A is held in a central position by means of six pieces of carbon; all intervening space is filled up with disks of heavy asbestos, cut in suitable dimensions.

---

[1]) For higher temperatures it must be recommended, to prepare this central part of the furnace from nickel, or to coat it heavily with gold; for the highest temperatures (up to 1600 C°.), *alundum*-cores of the *Norton Company* in *Worcester* (Mass.) U. S. A., are an excellent material.


I
U
K
Q₁
S
W
Q₂
Th
a
f
R
m₁
o
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v₁
z
M
N
v₂
s₂
m₂
d
a
A
Q₂
K
K
W
W
Q₁
P
V
V
D
+
−
B
4/5 full size

Fig. 1.

The core A possesses a somewhat thinner wall at d, and is conical excavated on the lathe, as indicated in the figure 1, with the purpose to give the rather strongly deviating RÖNTGEN-rays an opportunity to reach the photographic plate without an interposing obstacle. The furnace-chamber must be kept at a constant temperature however; therefore it is necessary, to shut it at M, and like-wise the cover Q_3, to protect the photographic plate from heat-radiation, at N_1 by means of a thin plate of aluminium, which can be fixed or removed by means of a copper-ring. In this way the heat is sufficiently kept in the chamber, while the aluminium-screens do not interpose any appreciable obstacle in the way of the RÖNTGEN-rays. The aluminium screens have, at o, only a hole to introduce the thermoelement Th into the furnace. The crystal-plate p to be investigated, is fixed in position on a removable support, which can be adjusted in the furnace-chamber by means of the buttons m_1 and m_2, and a bayonet-joint under the screws s_1 and s_2, The crystal is fixed on the support by means of the two metal springs v_1 and v_2. The furnace-coil can bear a maximum current of 5,5 Ampères; with this intensity a temperature of 800° C. or somewhat higher, can be reached.

The connection of the furnace with the RÖNTGEN-apparatus was made in the following way. A brass plate was fixed in a vertical position on a long horizontal rail; against the vertical end of the plate a heavy lead-screen was fixed. In the brass plate a long brass tube of about 7 c.m. is fixed, and adjusted in a horizontal position; this tube bears at the side where the furnace stands, (i. e. at this side of the lead screen), a brass flange, which is turned off on the lathe in such a way, that the plane of its border is accurately adjusted perpendicularly to the direction of the emerging RÖNTGEN-rays. The tube R of the furnace just encircles the border of this flange. In the brass tube two cylinders of lead, about 5 m.m. long, are arranged at both terminals; they are fixed in such a way, that no rays can escape otherwise, than through the 1 m.m. broad central canals, which are pierced along the axes of the lead cylinders. As they are accurately adjusted so, that the axes of the two cylinders are lying in the same straight line, the direction of the bundle of RÖNTGEN-rays (about 1 m.m. in diameter) is wholly determined, as it were by means of a visor. Everywhere thick lead-plates are arranged so as to prevent the RÖNTGEN-ways from escaping otherwise, than through the narrow canal.

The furnace, with its axis in horizontal position, is now connected with the RÖNTGEN-apparatus, by pushing the tube R over the flange;

by a semi-cylindrical support, attached to the horizontal part of the brass plate, it is borne up from beneath, while a copperwire, wrapped round the double-walled cylinder of the furnace, helps to keep the apparatus in its position. It is necessary of course, to adjust the horizontal axis of the furnace exactly in the same level as the small canal for the emerging rays. The whole arrangement of the Röntgen-tube, the lead screen, etc., corresponds principally with that described formerly by one of us.[1])

§ **3.** *The material.* The *boracite,* used in this investigation, was from Sehnde, in Hannover. It crystallized in clear, pale blue-green large crystals, showing the form {110}. Two planeparallel plates were cut from a crystal, one perpendicular to a binary, the other one perpendicular to a ternary axis of the apparent regular form.

Our experiments were only made with a plate, cut perpendicular to a binary axis; at the same time such a plate must be perpendicular to a quaternary axis of the Bravais' space-lattice, if the crystal is really of the regular system.

By microscopic investigation the strong birefringence of the crystal-plate was easily demonstrated. It showed a typical polysynthetic structure; between crossed nicols it was in no position totally dark, but only locally. The composing lamellae showed high interference-colours; in convergent polarized light an interference-image of a biaxial crystal, almost perpendicular to an optical axis, was visible, with a dispersion, which would be in agreement with rhombic symmetry.

When the crystal-plate was heated in the microscope-furnace, already described by one of us, — in which furnace the crystal rests on the hot junction of the used thermoelement, — the polarisation-colours between crossed nicols change gradually from violet to yellow, blue and grey; then the field of the microscope gets dark *suddenly* at 266° C. On cooling the birefringence returns as *suddenly* as it disappeared; *it is an extremely remarkable fact, that almost the same lamellae return on that occasion, which were present already before heating.*

The experiment can be repeated arbitrarily; *thus we are quite sure, that in our experiments at fully* 300° *C. the optically isotropous form has always been present, while the birefringent one must have returned always after cooling to room-temperature.*

§ **4.** Our experiments now were made in such a way, that first a Röntgen-photograph was taken, when the crystal-plate was out

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[1]) H. Haga, Ann. d. Physik (4). **23**. 439, 440. (1907).

of the furnace. Then the plate was fixed into the furnace, this was heated to fully 300° C. and left at this temperature during one hour; only after that time, the second photograph was taken. When the furnace had cooled down to room-temperature, a third photograph was taken, while the plate remained in the furnace and in the same position, as during the heating of it. The time of transmission of the Röntgen-rays was 2 or 3 hours; this was shown to be sufficient, if a phosphorescent screen behind the photographic plate was used. The temperature of the furnace was under continuous control by means of the thermoelement *Th.* The obtained results were as follows.

Let us study first fig. 3 [1]); it represents the image, obtained at 300° C. The crystal-plate was 1 m.m. thick, and was fixed at a distance of 61 m.m. from the photographic plate. Notwithstanding the fact, that the normal of the crystal-plate did not coincide absolutely with the normal on the face of the hexahedron, one can conclude from it, that the diffraction-pattern possesses a *quaterny* axis of symmetry, — just what might be expected in each of the three possible Bravais' space-lattices of the regular system.

In fig. 4 the pattern is reproduced, obtained after the furnace has cooled down to room-temperature. The image is analogous to that of fig. 3 in a misleading way; however it doubtless differs from it. Especially the following facts may be brought more into the foreground: 1. in the quadrants to the right above and to the left below, in the first row of spots from the centre, there are found *three* small spots in close vicinity to each other; while at the same place in the opposite quadrants only *two* of these are present; 2. especially in fig. 2 it is very evident, that in both the rows, which are most elongated from the centre, there are only *five* spots between the two dark limiting ones, if the rows are situated at the opposite ends of a vertical diameter of the plate; but in the corresponding rows at the opposite ends of a horizontal diameter of the pattern, there are about *nine* spots between the two darker ones, while the spot in the midst of the row is darker than the others, and on both sides accompanied by a feebler spot. On the original negative of fig. 4 these differences could already be seen easily; but much better in the fig. 2, which represents the pattern obtained from a boracite-plate, 1,8 m.m. thick, but at a distance of only 42,5 m.m. from the photographic plate. Notwithstanding the fact, that this plate was not cut absolutely parallel to the face of the hexahedron; however, the

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[1]) We regret that the figures are only poor reproductions of the original röntgenograms, so that some details cannot be distinguished on them.

above mentioned differences can easily be stated. Another point of divergence of the figs. 3 and 4, which however does not relate immediately to the difference in period of the symmetry-axis, — is the fact, that in the fig. 4 (also in fig. 2), there are always two spots in the third row from the centre, which spots are missing wholly in fig. 3. We must conclude from this, that, notwithstanding the misleading analogy of figs. 2 and 4, with respect to fig. 3, the former two do not possess more than a *binary* axis of symmetry; with respect to the fact, that most observers contribute rhombic symmetry to the composing lamellae, it must be considered as highly probable, that this binary axis of symmetry corresponds really with a molecular arrangement of rhombic symmetry. In any case with a space-lattice, which is relatively close to a regular arrangement: for, as already mentioned, it was impossible till now, to state goniometrically any deviation of the pure regular crystal-form. However, the Röntgenogram shows this deviation with certainty, may it be only by small differences, while a misleading similarity or analogy with true regular symmetry remains present. This fact proves, that in problems of this kind, in many cases the method of the RÖNTGEN-patterns will be of higher value, than the different methods used up to this date.

§ **5**. The described experiments have thus demonstrated the fact, that by heating to 266° C., simultaneously with its optical isotropy, the boracite shows a slight molecular re-arrangement. The question, if the dimorphism of the boracite is connected with a change in its molecular arrangement, must, after what is found here, doubtlessly be answered in the affirmative. [1])

It makes only little difference or none in this question, whether the obtained images correspond perhaps only to the exclusive action of one single kind of the atoms, constituting the chemical molecule of boracite. For every kind of atoms of the molecule must be the structure-unit of an individual space-lattice, and all those intergrown space-lattices must be either congruent, or equal with respect to

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[1]) Remarkable is also the *granular* character of the central spot on these photographs: experiment taught us, that this fact is connected with the presence of the two aluminium-screens *M* and *N* in the way of the RÖNTGEN-rays. Especially remarkable is the more or less regular hexagonal of hexaradiant shape of these spots. Such an hexagonal image was also obtained by means of a thin aluminiumplate alone, about 1,55 m m. thick. It is not improbable, that this fact is connected in some respect with the octahedral crystalform of the aluminium; perhaps the hexagonal image corresponds to six octahedron-faces as directions of preference for the RÖNTGEN-rays.

their symmetry, and at least in conformity with each other, with rational proportions of their linear distances; and they must also remain so, if their aggregation shall be crystallographically a possible one. For that reason the changes in symmetry of one of these space-lattices, must be connected with the same changes in the other ones; it can hardly be hazardous, to conclude from the changes in the Röntgenogram of one of them, with regard to the changes of the other space-lattices. Besides it will seem somewhat improbable with respect to the relatively slight change in molecular arrangement, that at the same time no further change should accompany it, which takes place within the domain of the composing molecules themselves. For the birefringence is, even just a little below the inversion-temperature, again very strong, but disappears at 266° C. quite suddenly. It is difficult to believe, that so great a change could only be attributed to the apparently not very great change in the molecular arrangement. The conception, that the optical properties partly, if not greatly, must be caused by the anisotropy of the composing molecules themselves, more than by the structure of their molecular aggregation, is often defended, just because it is able to give a clear idea of the nature of optically-anomalous crystals. It is true, our experiments have once more proved, that doubtlessly the influence of the molecular arrangement is present; but perhaps it is in this direction of research, that the cases are to be found, which will allow a definitive conclusion with respect to the one or the other of those views.

Experiments with *leucite*, in which the difficulties will be even greater, because of the higher inversion-temperature and the much slower transformation, are at present being made in our laboratories.

Groningen, January 1914.

Mineralogy. — "*On temperature-measurements of anisotropous bodies by means of radiation-pyrometers.*" By Prof. Dr. F. M. Jaeger and Dr. Ant. Šimek. (Communicated by Prof. Haga).

(Communicated in the meeting of January 31, 1914).

§ 1. In the study of the optical behaviour of white-hot silicates, it accidentally happens that the temperature of the investigated objects is measured by means of the now generally used radiation-pyrometers of Wanner or of Holborn—Kurlbaum.

The temperature of the body, as determined in this way, generally cannot coincide with its real temperature; for the mentioned pyrometers will indicate only that temperature, which an absolutely black body should possess, to show the same emission, that really is observed by means of the pyrometer. Just because different objects differ from the absolutely black state in an unequal degree, they will seem to possess different radiation-temperatures, when heated to the same temperature of t° C.

If the radiating object, as in the case of birefringent crystals, is anisotropous with respect to its absorption for radiant energy, it must be also anisotropous with respect to its emission, in accordance with KIRCHHOFF's fundamental law. Such a radiant anisotropous body will behave therefore as if it had different temperatures in different directions of vibration; its apparent radiation-temperature will not be the same for different vibration-directions of its emitted radiation.

§ 2. Although this conclusion from KIRCHHOFF's law of radiation, has been tested already occasionally by means of experiment[1], — as we learned however just after this investigation was finished, — all those experiments were made at a time, when the construction of radiationpyrometers, founded on the law of KIRCHHOFF, and on those of WIEN and PLANCK formulated since that date, had not yet taken place: We thought it interesting, to demonstrate the said phenomenon once more by means of a radiationpyrometer, as it is used now in a very perfectly develloped form in all laboratories for high temperature work, and thus to show at the same time again the validity of KIRCHHOFF's law, in qualitative respects, by means of a striking experiment.

§ 3. Our experiments were made in the following way.

From a crystal of dark green turmaline of *Brasil*, two small flat cylinders of about 1 mm. thickness were prepared; one of them had its axis parallel to the crystallographical axis of the trigonal mineral, the other one perpendicular to it. The form of a cylinder was chosen,

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[1] KIRCHHOFF himself (Pogg. Ann. **109**, 299. (1860)), has already drawn this conclusion from his theory, and tried to demonstrate it by experimenting with a heated turmaline-crystal. The same experiment was repeated later on by BALFOUR STEWART (Phil. Mag. (4). **2**, 391. (1861)). Although both experiments can be considered as proving the fact, they are not adapted to make a strong impression. In 1902 however the law of KIRCHHOFF for this case was demonstrated in a convincing and quantitative manner by PFLÜGER (Ann. d. Physik (4). **7**, 106 (1902)), who measured by means of a spectrophotometer, as well the difference in absorption for the ordinary and extraordinary lightwaves, as the difference in emission of white-hot turmaline for vibrations in the direction of the crystallographical axis, and for those perpendicular to it.

to make the heat-transport between it and the walls of the furnace as symmetrical as possible. The cylinders, which had a diameter of about 2 or 3 mm., were carefully polished, and they were fixed in the small resistance-furnace *B* (Fig. 1) by means of a fine platinum-wire, wrapped round their curved surfaces; the furnace was of the type, used in this laboratory for microscopical purposes, and described more in detail by one of us on another occasion [1]).

By means of the fine platinum-wire the small cylinder was fixed just above the junction of the thermoelement *E*, made of platinum-platinumrhodium, and used in this furnace as the crystalsupport;

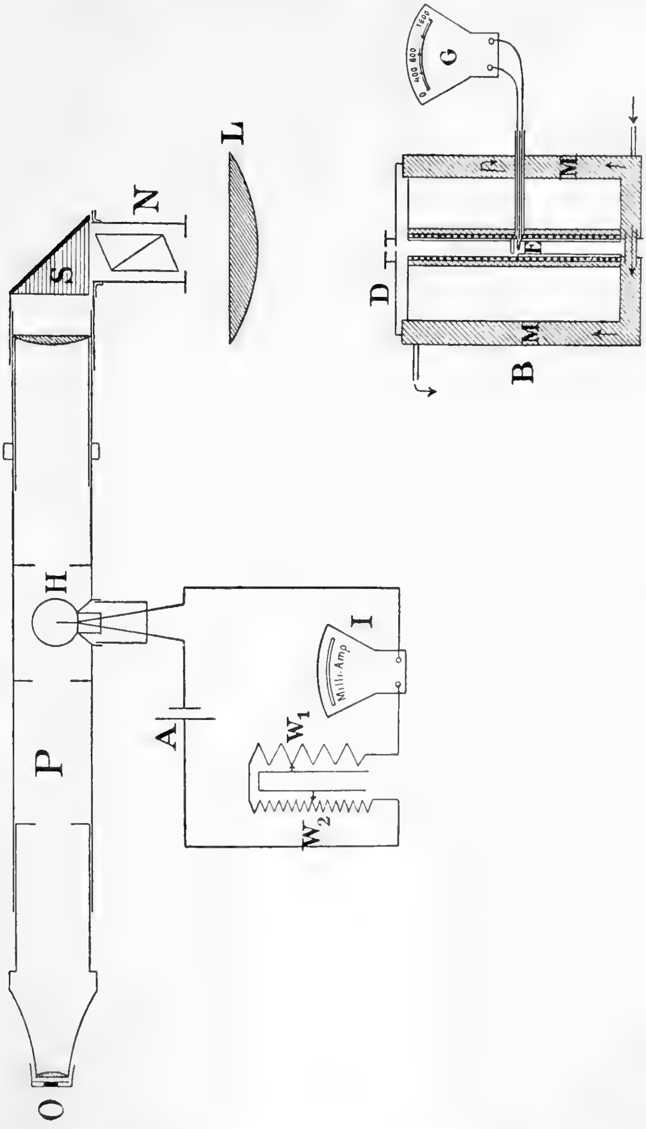

Fig. 1.

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[1]) F. M. **Jaeger**, Eine Anleitung zur Ausführung exakter physiko-chemischer Messungen bei höheren Temperaturen; Groningen (1913), pag. 102, 103.

this thermoelement was connected with a sensitive direct-reading galvanometer *G*. The furnace had an inside-winding of platinum-wire; it was surrounded by a hollow mantle *M*, in which continually a stream of cold water was circulating. It was heated with direct current of 220 Volt and 3—5 Ampères; the temperature was regulated by means of a rheostate in such a way, as to be kept constant at will at every height. The cylinder was fixed in such position, that it remained at all sides equidistant from the furnace-walls, and that it was situated in the very short part of the furnace, where no considerable fall of temperature along its axis, could be detected. Above the furnace a movable diaphragm *D* was present, to make an entrance to the measuring-apparatus possible only for the rays, coming from a very small part of the surface of the glowing cylinder; a plane-convex lense *L*, arranged above the furnace, allowed to observe a sharp image of every chosen part of the glowing cylinder-surface, by means of the telescope of the radiationpyrometer *P*.

This pyrometer *P* was of the HOLBORN-KURLBAUM-type, which is to be preferred to the about equally accurate pyrometer of WANNER, because of its giving an opportunity to observe the objects themselves in the hot furnace sufficiently well. Before the objective of the pyrometer, a total-reflecting prism (45°) *S* was fixed, whose hypothenuse-side was heavily coated with silver; it was fixed in an innerly blackened tube, which at the same time bore the rotating Nicol-prism *N*. This prism *N* could eventually be removed in an easy way, and, if necessary, be substituted by another prism *N'*, to be fixed this time however at the opposite end of the telescope, before the ocular. The telescope contained the accurately calibrated incandescent-lamp *H*, which was lighted by the current of two storage-cells *A*. In the same circuit were present two easily adjustable rheostates W_1 and W_2, and a milliampère-meter *I*, provided with pointer and scale.

The calibration of the incandescent-lamp *H* between 600° and 1000° C. gave the following results:

Temperature in ° C.:	Intensity of current in milli-ampères:	Number of milli-ampères, corresponding with a temperature-rise of 1° C.:
600°	318	0.38
700°	356	0.40
800°	396	0.44
900°	440	0.44
1000°	484	

Fig. 2.

For temperatures under 800° C. it makes evidently no difference for the adjustment of the pyrometer, if a monochromatic red glass is placed before the ocular, or not. The way, in which the wire of the incandescent-lamp and the image of the heated cylinder could be observed after the diaphragm D was removed, is visible from fig. 2; the hot crystal there is indicated by p, while d represents the wire of the lamp.

§ 4. In first instance it was tried to find out, in what way this apparatus would show the properties of an isotropous radiator.

For the purpose to be as much as possible in analogous conditions as were present in the study of the expected phenomenon, these experiments were made with a turmaline-cylinder, with its flat end cut perpendicularly to the optical axis of the crystal. It could be proved easily, that this crystalsection, which was investigated at temperatures ranging from 800° to 1000° C. showed in all directions of vibration the same radiation-temperature: on rotating the nicol N, the intensity of the radiation was *the same* at every moment. This observation proves also, that no disturbing polarisation-phenomena were caused by the reflection of the light at the prism S; the observations to be described further-on are thus proved to be quite independent of the presence of this reflecting prism.

The object appeared, after removal of the nicol N, to possess considerably lower temperature, than the thermoelement indicated; the differences between 700° and 800° are about 12°—16° C., between 800° and 900° about 3°—12° C., between 900° and 1000° about 5° C. The indications of the galvanometer are therefore diminished by these amounts, to find the true temperature of the object. Those lower temperatures are probably partially caused by the fact, that the small, but relatively thick cylinder was fixed at some distance above the hot junction of the thermoelement, while a considerable heat-conduction took place along the suspension-wires. The turmaline-plate, cut perpendicularly to the optical axis, got soon opaque at a temperature of 900° or 1000° C.; the cylinder however, which was cut parallel to this axis, remained transparent at 1000° C. for a long time, so that it was possible to see the hot junction of the thermoelement through it, although only very feebly. Finally however also this section got opaque: the investigations with HAIDINGER's dichroscope e.g., are made all with such an opaque cylinder. Because of the very steep temperature-fall in these small furnaces, the parts of the furnace before and behind the radiating object were for the greater part considerably cooler than the turmaline-plate itself.

§ 5. After it was demonstrated in this way, that the chosen apparatus was really suitable, to make accurate temperature-readings, the other cylinder, cut parallel to the crystallographical axis, was fixed into the furnace in quite the same way. By a preliminary optical investigation the direction of maximum light-absorption was fixed, which direction we will discern as R_m. The emitted light is elliptically polarised; the intensity of the radiation for vibrations in the two principal directions could be studied easily by rotating the nicol N.

a) In the field of the telescope, R_m may be in a vertical position. The polarisator had its plane of vibration parallel to R_m; reading at 739° C.: 350 M.A. If the polarisator N is rotated over 90°, the intensity of the current in the incandescent-lamp is only 344 M.A. at 739° C. When the nicol is rotated over 360°, the following readings were made in the four principal situations: 350 M.A.; 344 M.A.; 351M.A.; 346 M. A.; finally once more: 351 M. A.

The apparent temperature of the small cylinder with respect to vibrations in the direction of maximum absorption thus seems to be clearly higher for 14° or 15° C., than in a direction perpendicular to the first.

b) Now R_m was in a horizontal position; the plane of vibration of the prism N is vertical. At 751° C. the readings were now: 351M.A., and after N being rotated over 90°, —356 M. A.

c) R_m is replaced as in *a*); the polarisator has its plane of vibration parallel with R_m. Readings: at 756° C., first 358 M.A., and after rotating N over 90°: 352 M. A.

d) R_m is again horizontal. At 815° C. the readings of the milliampèremeter are: 376 M.A. and 381 M.A., according to the plane of vibration of N being perpendicular to, or parallel with R_m.

e) R_m is now in a vertical position. Readings at 826° C.: 388 M.A. and 383 M.A. If the nicol is removed, then the reading is in all directions: 402 M.A.; the apparent increase of temperature is of course explained by the light-absorption of nicol-, and prism-system. Therefore all numbers of M.A., as they are found, need to be augmented with 20 M.A., to get the true radiation-temperatures (Table).

f) The experiments mentioned *d* and *e* were now repeated, with the use of a red, almost monochromatic glass on the ocular. As the same readings were made as before, there seems to be no difference of any appreciable amount between the two modes of observation.

g) If all nicols are removed, as well before as behind the pyrometer, the readings remain the same, if the furnace is turned over some angle by means of the table of the microscope. Once more thus the reflection at the prism S is demonstrated to have no real effect on the results.

h) A nicol N' is adjusted behind the pyrometer, and while R_m has a fixed position, it is turned over 0°, 45°, and 90° respectively. The readings at 850° C. were:

Rotation of N' over:	*Milli-Ampères:*
0°	415
45°	413
90°	409

i). Finally the nicol N was placed again before the pyrometer and of course the other one was removed. At 898° C. the readings were now: 418 M. A. and 410 M. A.; at 963° C in the same way: 441 M.A. and 447 M. A.

We can thus conclude from it:

True temperature of the body in ° C.:	Readings in M. A. as they would be without the absorption by the nicol:	Radiation-temperatures for vibrations in the two principal directions:	Differences:
	R_m : $\perp R_m$:	R_m : $\perp R_m$:	
739°	370 en 364	735° en 720°	15°
751	376 „ 371	750 „ 737	13
756	378 „ 372	755 „ 740	15
815	401 „ 396	811 „ 800	11
826	408 „ 403	824 „ 816	8
850	415 „ 409	846 „ 831	15
890	435 „ 429	889 „ 875	14
898	438 „ 430	895 „ 878	17
969	467 „ 461	961 „ 948	13
		Mean:	13°.5 C.

§ 6. It needs to be remarked, that from the individual differences in sensitiveness of the human eye, evidently there result greater or smaller values, than those given in column 4, if different observers try to determine at the same time the apparent temperature-differences between R_m and the direction perpendicular to it. So one of us always found somewhat *greater* values, than the mean value of column 4. But the difference itself as a real phenomenon remains without any doubt.

§ 7. Finally we made also an experiment, in which the apparent colder and hotter parts of the turmaline made the impression of being in immediate contact with each other, and therefore could be compared immediately, so that the phenomenon gets in this way exceedingly striking.

The furnace was now fixed in a horizontal position, with its central axis in the direction of the optical axis of the telescope; the total reflecting prism can be removed in this case. Before the objective of the pyrometer, instead of the nicol N, a Haidinger dichroscope-ocular was adjusted in such a way, that two images, an ordinary and an extraordinary one, of a small part of the crystal-surface, were obtained; the object made therefore the impression of being divided into two halves.

If all the circumstances of the experiment, e.g. the reversing effect of the telescope, etc., were considered, it could be demonstrated, that in the upper field only light was transmitted with a horizontal vibration-plane, in the lower one only that with a vertical plane of vibration; the last appeared to be the light of the extraordinary waves. In the fig. 3 these vibration-directions are indicated by the shadowing of the fields.

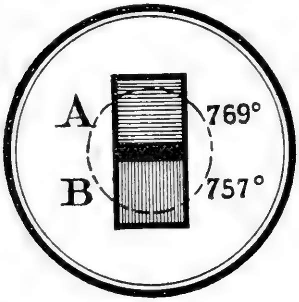

Fig. 3.

The temperature-measurements in both images, — which could be performed in an easy way, because the image of the lampwire, on moving the eye before the ocular, was seen by paralaxis now in the upper, now in the lower field, — demonstrated, that at 769° C. the lower field appeared to have a radiationtemperature of 757° C., the upper one however of 769° C. In concordance with the well-known fact, that a turmaline-plate, if parallel with the crystallographical axis, principally transmits only the light of the extraordinary waves, which are vibrating *in* the principal optical section of the crystal, — thus the direction of the horizontal vibrations (i.e: of the ordinary waves), is at the same time the direction of maximum light-absorption.

As the field A corresponds thus with that direction of vibration, wherein the maximum absorption of the radiant energy takes place, so the apparent temperature must also seem higher in that field, — quite in accordance with the law of KIRCHHOFF.

Groningen. *Laboratory for Inorganic and Physical Chemistry of the University.*

Chemistry. — *"Allotropy and electromotive Equilibrium."* By Prof. ERNST COHEN.

(Communicated in the meeting of January 31, 1914).

In the address on allotropy which I delivered on May 16th 1904 at the opening of the VAN 'T HOFF-Laboratory at Utrecht (this adress has been published as a pamphlet and also in the "Chemisch Weekblad" [1])) I called the attention of my audience to the importance of a systematic study of this phenomenon. I also gave an outline of the way to be followed in continuing the researches I had carried out with my collaborators in this direction since the year 1899.

Since that time Mr. SMITS at Amsterdam has also chosen allotropy as a field of work. Into that matter I shall not enter further at present.

However attention may be called to the form which characterizes Mr. A. SMITS' publications and which may give rise to a misunderstanding.

This is strikingly shown in his paper in these Proceedings Vol. 16, p. 708 (meeting of Dec. 27, 1913) where he says:

"In connection with the foregoing it is desirable to draw attention to this that according to these considerations *the contact with the solution of a salt of the metal must have an accelerating influence on the setting in of the internal equilibrium of the metal.*"

Mr. A. SMITS has written these words in italics; he has however forgotten to mention in the text or in a footnote that this fact was discovered and published 15 years ago by ERNST COHEN and C. VAN EYK in their researches on the allotropy of tin [2]).

Moreover he forgets to point out that an explanation of this

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[1]) Chem. Weekbl. **1**, 481 (1903/04).

[2]) Zeitschr. f. physik. Chem. **30**, 601 (1899).

phenomenon which is common knowledge now-a-days (and which is mentioned even in elementary textbooks) was given by me 15 years ago[1]) and that I myself and my collaborators made use of it in our recent researches on the allotropy of bismuth, cadmium, copper and zinc.

The quotation reproduced above is so striking that discussion of the other instances of the same kind is unnecessary.

I have always intended to abstain from any remarks on this point. But as many colleagues both at home and abroad have taken increasing umbrage at the procedure of Mr. A. Smits, I feel myself reluctantly compelled to draw atttention to the matter.

Utrecht, van 't Hoff-Laboratory.
January 1914.

Physics. — "*A new relation between the critical quantities, and on the unity of all the substances in their thermic behaviour.*"

By J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of January 31, 1914).

1. In my latest paper[2]) I have treated some relations — also derived by van der Waals — in which a perfectly accurate form was substituted for the approximate one; I have proved that not any factor $\theta = f(v)$ by the side of ${}^{a}/_{v^2}$, so not the factor $(1-{}^{1}/_{2}x)^2$, added to it on account of the so-called quasi-association either, is able to account for the course of the function $\varphi = \frac{f-1}{f_k-1} \cdot \frac{\varepsilon_{coëx.}}{d_1 d_2}$ in the neighbourhood of the critical temperature (§ 3); I think I have demonstrated that either a, or b, or both must be functions of the temperature (§ 4), and I have made a few more remarks about the form of the reduced equation of state (§ 5). Now I wish to make some remarks on the form of the dependence of the quantity b of the volume v.

The temperature dependence will be considered in a subsequent paper. I may, however, state already now that I have come to the conclusion that this dependence too must be exclusively looked for in b, whereas a is assumed to be independent of the temperature. Van der Waals seems finally also to have come to this conclusion, at

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[1]) Zeitschr. f. physik. Chem. **30**, 623 (1899).

[2]) These Proc. of Sept. 3, 1913, p. 44—59.

least I infer from an abstract in the Chem. Weekblad of Jan. 3, 1914, p. 29 of his most recent publication "Weiteres zur Zustandsgleichung" (summary of his latest Papers in these Proceedings of Nov. and Dec. 1912, Jan. and Febr. 1913), that he has adopted this opinion.

Thus the quantity b would control the whole thermic behaviour of the different substances, and the variability of this quantity in dependence on v, and also on T would be the cause that this actual behaviour deviates from that which would conform to VAN DER WAALS' *ideal* equation of state with a and b constant.

Further it seems to appear more and more that all the causes devised up to now, which were to account for the variability of b, yet jointly find their expression in one comparatively simple equation.

When the former supposition of perfectly hard and elastic spheres is abandoned for that of a *gradual* exchange of the energy during the collisions, in which at bottom the kinetic energy of the moving and colliding molecules may be thought transferred to the interjacent medium, which transition determines the external pressure — part of the foundation of the before assumed correction on account of *apparent diminution* is no longer valid, at least in its old form.

When the molecules are considered as pretty stable systems, the volume of which varies only slightly in consequence of the increase of the internal and the external pressure, a great part of the correction introduced later on account of the *real diminution,* must no longer be applied. We are led to this view when we consider how exceedingly slight the influence of the temperature is *just at higher temperatures* (we shall come back to this presently), so that it seems that the molecule systems are only slightly modified in volume even by the influence of the thermal motion (which will certainly be more intense than that of the pressure). The rise of temperature seems chiefly to have this influence that some molecules (the number of which is indicated by the wellknown thermodynamic relations) *suddenly* break up into simpler ones or the reverse), when the strong chemical bond is broken for *these* molecules in consequence of the too great intensity of the internal motions. Then in the "dissociating" substance there are simply *two kinds* of molecules, e.g. for N_2O_4 the molecules N_2O_4 and NO_2, but — *as long as they exist individually* — both seem to be pretty insensible to changes of volume by temperature or pressure.

And finally — when the so-called *quasi-association* is considered as a phenomenon inherent in the nature of things: I mean in this sense that *temporary molecule aggregations* are naturally formed without any special cause, in consequence of collisions, and of the temporarily acting strengthened attractive forces, or by other accidental circumstances — so that this state of quasi-association[1] for every substance is quite determined by the value of the (reduced) temperature and of the volume — we are naturally led to combine all the influences mentioned into one equation $b=f(v,T)$, of which at present we only know the general form, without being able to define it more closely. It seems to me that the final decision — as regards the derivation of the equation in question — will be given again by the radiation theory and the theory of quanta.

2. Before giving the new relation between the critical quantities, found by me some time ago, we may briefly state the results of the foregoing paper, as far as the relations existing between the critical quantities are concerned.

When $b=f(v)$ is assumed, and $\left(\frac{\partial b}{\partial v}\right)_k$ and $\left(\frac{\partial^2 b}{\partial v^2}\right)_k$ is indicated by b'_k and b''_k, putting $v_k : b_k = r$, it follows from the equation of state

$$p=\frac{RT}{v-b}-\frac{a}{v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

in the first place, by putting $\left(\frac{dp}{dv}\right)_T$ and $\left(\frac{d^2p}{dv^2}\right)_T=0$ (loc. cit. p. 45 et seq.):

$$\frac{r-1}{r}=\frac{2}{3}\,\frac{1-b'_k}{1-{}^1\!/_8\beta''_k} \;, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

when $\beta''_k = v_k\, b''_k : (1-b'_k)$.

Further

$$\left.\begin{aligned} RT_k &= \frac{8}{27}\lambda_1\frac{a}{b_k}\,, \text{ in which } \lambda_1=\frac{27}{8}\,\frac{(r-1)^2}{r^3}\,\frac{2}{1-b'_k} \\ p_k &= \frac{1}{27}\lambda_2\frac{a}{b_k^2}\,, \quad\;\; ,, \qquad\; \lambda_2=\frac{27}{r^2}\left[\frac{r-1}{r}\,\frac{2}{1-b'_k}-1\right] \end{aligned}\right\} \quad . \quad . \quad (2)$$

In this λ_1 and λ_2 are never far from 1; for substances that deviate most from those which would correspond to the ideal VAN DER WAALS's equation of state — the latter will henceforth be called "ideal substances" for shortness — λ_1 and λ_2 are both $=0{,}98$.

For the so-called critical coefficient $s=RT_k : p_k v_k$ is found:

$$s=\frac{\lambda_1}{\lambda_2}\,\frac{8}{r}\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which $\lambda_1 : \lambda_2$ may always be put $=1$.

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[1] Which according to this view has therefore *nothing* to do with *real* association, as for NO_2 and H_2O, which is of entirely *chemical* nature.

If $p:p_k=\varepsilon$, $T:T_k=m$, $v:v_k=n$, $b:v_k=\beta$ may be put, the reduced equation of state, in consequence of the mentioned relations, becomes:

$$\left(\varepsilon+\frac{27:\lambda_2 r^2}{n^2}\right)(n-\beta)=sm \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Another set of equations is found by the introduction of the critical pressure coefficient $f=\left(\frac{T}{p}\frac{dp}{dT}\right)_k$. But in this the dependence on the temperature of the quantity b must be taken into account. We easily find (see p. 56—57 loc. cit.):

$$f=\frac{RT_k}{p_k(v_k-b_k)}\left(1+\frac{v_k}{v_k-b_k}\beta'_t\right),$$

when β'_t represents $\frac{T_k}{v_k}\left(\frac{\partial b}{\partial T}\right)_k$. Hence this becomes:

$$f=s\frac{r}{r-1}\left(1+\frac{r}{r-1}\beta'_t\right).$$

If now the temperature-correction $\frac{r}{r-1}\beta'_t$ is represented by φ, and if we bear in mind that $s\frac{r}{r-1}$ would be the value of f, when b (or a) were *no* function of the temperature, which value we shall henceforth denote by f', we have the relation:

$$f'=s\frac{r}{r-1}=\frac{\lambda_1}{\lambda_2}\frac{8}{r-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which

$$f'=\frac{f}{1+\varphi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In this f is therefore the quantity $\left(\frac{d\varepsilon}{dm}\right)_k$ determinable *experimentally*, which, however, will not appear as such in the different relations. In them f' occurs systematically, which is connected with f by the relation (5). Fortunately, however, φ is always very small, so that in a first approximation f may be substituted for f'. But for the sake of accuracy we have everywhere in what follows not identified f' with f.

When $p_k+{}^a/_{v_k^2}$ is substituted for $RT_k:(v_k-b_k)$

$$f'-1=\frac{1}{\lambda_2}\frac{27}{r^2}=\frac{\lambda_2}{\lambda_1^2}\frac{27}{64}s^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

follows from $f'=RT_k:p_k(v_k-b_k)$, so that we have also the relations:

$$r=\frac{3}{\sqrt{\lambda_2\frac{f'-1}{3}}}\quad ; \quad s=\frac{8}{3}\sqrt{\frac{\lambda_1{}^2}{\lambda_2}\frac{f'-1}{3}}, \quad . \quad . \quad . \qquad (6a)$$

while now the reduced equation of state may be written:

$$\left(\varepsilon+\frac{f'-1}{n^2}\right)(n-\beta)=sm, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (c)$$

in which f' will always be *slightly* smaller than f.

3. If we assume for an "*ordinary substance*" (which is therefore farthest from the above mentioned "ideal substance") $s=3{,}77$ [1]), hence $^1/_s=0{,}2653$, then the value $\underline{2{,}12}$ corresponds to this for r, with $\lambda_1:\lambda_2=1$ according to (3).

Then the value $\underline{7{,}136}$ is found for f' from (4) with $r:(r-1)=1{,}893$. Since f will have to be somewhat greater than f', as in (5) φ is positive at any rate, but as for f experimentally a value is found which for the said substances if not very near 7,14, yet lies only little higher, we see confirmed here what I observed already above (see also loc. cit. p. 57), that φ will be exceedingly small at the critical temperature, and that therefore f' and f will differ very little.

Further follows from $f'-1=27:\lambda_2 r^2$, with $27:r^2=27:4{,}494=$ $=6{,}008$, for λ_2 the value $0{,}979=\underline{0{,}98}$.

And from $f'=(\lambda_1:\lambda_2)\times(8:(r-1))$ the value $0{,}999=1$ for $\lambda_1:\lambda_2$ is then properly found back with $8:(r-1)=7{,}143$, after which $\underline{0{,}98}$ is also found for λ_1.

The quantities λ_1 and λ_2 will vary between 0,98 and 1, according as one descends from "ordinary substances" to "ideal substances" through the whole region of substances. In this r will at the same time vary from 2,12 to 3; s from 3,77 to 2,67, and f from 7 to 4.

We further find for the relation for λ_1 indicated in (2):

$$1-b'_k=\underline{0{,}9085} \quad ; \quad b'_k=\underline{0{,}0915}.$$

The value of β''_k may be calculated from (1). We then find:

$$\beta''_k=v_k b''_k:(1-b'_k)=\underline{-0{,}4398} \quad ; \quad v_k b''_k=\underline{-0{,}3996}.$$

In the above we only *apparently* started from one fundamental quantity, viz. s, from which we have calculated $r=2{,}12$. For we then made use of the circumstance that $\lambda_1:\lambda_2=1$ may be put.

Strictly speaking we ought to have assumed *two* quantities, viz.

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[1]) Mean of the values 3,766 for *n*-Pentane, 3,735 for *i*-Pentane, 3,796 for Fluorbenzene.

s and r, from which all the other quantities can then be calculated. For r we could then have *assumed* 2,12, and we had then *found* $\lambda_1 : \lambda_2 = 1$. But it is better to start from two quantities, which are *experimentally* determinable. And for the present s and f' seem the most suitable, even though s depends on the accurate determination of the *critical density* (which is often very difficult, and generally takes place through the strictly speaking unpermissible prolongation of the so called "straight diameter" — unpermissible, because this straight diameter exhibits a perceptible curvature *close* to the critical point), and though the determination of f' (supposing we may put $f' = f$) is from the nature of the thing always connected with not very accurate calculations of pressure and temperature *differences* close to the critical point.

We might e.g. have assumed $s = 3{,}77$ and $f = 7$, and we had then also found $\lambda_1 = \lambda_2 = 0{,}98$. And the equality of λ_1 and λ_2 would also have become clear for other substances, as Oxygen, Argon etc., where another set of values for s and f had been started from.[1]

We shall, however, immediately see that in consequence of the new relation found by me instead of f' and s another quantity can be introduced, which in contrast with the two mentioned ones is experimentally pretty sharply definable. We mean the direction of the *straight diameter*, which can be determined very accurately from observations even far below the critical temperature, and is at any rate not affected by any uncertainty in the observations *close to* the critical temperature. T_k and v_k will, indeed, of course be of influence in the determination of the "reduced" coefficient of direction.

If, as said, we take, however, for the present f' and s, we find easily from the above relations:

$$r = \frac{f'}{f'-s} \quad ; \quad r - 1 = \frac{s}{f'-s} \quad . \quad . \quad . \quad . \quad . \quad (\alpha)$$

Further from $f' - 1 = 27 : \lambda_2 r^2$ and $f' = (\lambda_1 : \lambda_2) \times (8 : (r-1))$:

$$\lambda_1 = \frac{27}{8} \frac{s}{f'-1} \left(1 - \frac{s}{f'}\right) \quad ; \quad \lambda_2 = \frac{27}{f'-1} \left(1 - \frac{s}{f'}\right)^2 , \quad . \quad . \quad (\beta)$$

through which:

$$\frac{\lambda_1}{\lambda_2} = \frac{s}{8\,(1 - {}^{s}/_{f'})} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\gamma)$$

Finally we shall find:

$$1 - b'_k = \frac{2\,s\,(f'-1)}{f'^2} \quad ; \quad -\beta''_k = -\frac{v_k b''_k}{1 - b'_k} = \frac{f'-4}{f'} \quad . \quad (\delta)$$

In this particularly the last relation, viz. for β''_k, is remarkably simple, the more so as there occurs only one quantity, viz. f', in it. For $f'=f=4$ we have $\beta''_k=0$, as we should have.

4. If we may really put $\lambda_1:\lambda_2=1$, s is perfectly determined by f' through the relation (γ), and only one quantity either s or f' suffices. Then we have only to put:

$$s=\frac{8f'}{8+f'} \qquad \text{or} \qquad f'=\frac{8s}{8-s}$$

everywhere in the above. Further in (3) rs simply becomes $=8$ and in (4) f' will become $=8:(r-1)$.

Hence if we express everything in f', we have:

$$\left.\begin{array}{c} s=\dfrac{8f'}{8+f'} \quad ; \quad r=\dfrac{8+f'}{f'}=1+\dfrac{8}{f'} \quad ; \quad \lambda=\dfrac{27f'^2}{(f'-1)(8+f')^2} \\ 1-b'_k=\dfrac{16(f'-1)}{f'(8+f')} \quad ; \quad -\beta''_k=\dfrac{f'-4}{f'} \end{array}\right\} , \qquad (7)$$

by the side of which we mention a few more earlier relations in the new form:

$$\left.\begin{array}{c} rs=8 \quad ; \quad f'(r-1)=8 \quad ; \quad \lambda(f'-1)=\dfrac{27}{r^2}=\dfrac{27}{64}s^2 \\ r=3:\sqrt{\lambda(f'-1):3} \quad ; \quad s={}^8/_3\sqrt{\lambda(f'-1):3} \end{array}\right\} , \qquad (8)$$

when $\lambda_1=\lambda_2$ is represented by λ. We once more point out, that all the foregoing relations hold quite generally and perfectly accurately, but that the relations (7) and (8) will be dependent on the assumption $\lambda_1:\lambda_2=1$. But this latter relation may be considered as perfectly accurate.

Now

$$RT_k=\frac{8}{27}\lambda\frac{a}{b_k} \quad ; \quad p_k=\frac{1}{27}\lambda\frac{a}{b_k^2} ,$$

is simply found for RT_k and p_k, so that we can calculate the quantities a and b_k very accurately from the observed critical pressure and temperature.

As for the quantity λ, it is $=49:50=0{,}98$ for $f'=7$; for $f'=6$ we find $243:245=0{,}992$; for $f'=5$ we have $\lambda=675:676=0{,}9985$, and for $f'=4$ the value 1 is found. So whereas $\lambda_1:\lambda_2$ is pretty accurately $=1$, $\lambda=\lambda_1=\lambda_2$ will in the utmost case *only* deviate 2 °/₀ from unity, and will approach more and more to 1 for substances with lower values for f'.

Let us now proceed to give the new relation and at the same time introduce the reduced coefficient of direction of the straight diameter γ.

5. *A new relation.*

I found, namely, that remarkably enough, there always exists a simple relation between the quantities $r = v_k : b_k$ and $z = b_k : v_0$. *Not* the *approximate* equality of s and $s' = v_k : v_0$, brought forward by van der Waals, but another *accurate* relation. For though s differs little from s', yet the difference can amount to $^1/_8$ of the value, whereas the relation found by me seems perfectly accurate; the value of $s : s'$ can be calculated from it for every value of the chosen independent parameter.

We know that according to the property of the "straight diameter"

$$\frac{\frac{1}{2}(d_1 + d_2) - 1}{1 - m} = \gamma,$$

when d_1 and d_2 represent the reduced densities of liquid and vapour. When d_2 may be neglected with respect to d_1, we have simply:

$$\tfrac{1}{2} d_1 = 1 + \gamma (1 - m),$$

which for $m = 0$ would pass into $\frac{1}{2} d_0 = 1 + \gamma$ or

$$d_0 = \frac{v_k}{v_0} = 2 (1 + \gamma).$$

Here v_0 is therefore the fictitious *extrapolated* liquid volume at the absolute zero-point; this volume can of course not be realized for liquids, but in this ideal limiting case we may write b_0 for it — by b_0 we must, therefore, understand the same thing as is understood by v_0, i.e. the smallest volume that a number of molecules lying closely together, so that they are all in contact with each other, can occupy.

So if in future we represent the relation $v_k : v_0$ by s', and the relation $b_k : b_0$ by z, we have:

$$\frac{v_k}{b_0} = s' = 2 (1 + \gamma); \quad \frac{b_k}{b_0} = z = \frac{s'}{r} = \frac{2 (1 + \gamma)}{r} \quad , \quad . \quad . \quad . \quad (9)$$

because $r = v_k : b_k$. So far these equations do not contain anything new; the last may serve to calculate z, when γ and r are known, in which r may be calculated from one of the equations (7), viz. $r = 1 + (8 : f')$. Thus $z = 1{,}8$ e.g. for an ordinary substance ($\gamma = 0{,}9$, $r = 2{,}12$); $z = 1{,}5$ for argon ($\gamma = 0{,}75$, $r = 2{,}33$); $z = 1$ for an ideal substance ($\gamma = 0{,}5$, $r = 3$).

But now I found that always:

$$\underline{z = \frac{2}{r - 1}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

for the most different substances. In this form the relation was first discovered by me. Thus among others:

For an ordinary substance	$(f' = 7{,}2)$	$1{,}8 = \dfrac{2}{1{,}11} = 1{,}8$
„ Argon	$(f' = 6)$	$1{,}5 = \dfrac{2}{1{,}33} = 1{,}5$
„ ideal substance	$(f' = 4)$	$1 = \dfrac{2}{2} = 1$

in which the value of z in the first member was calculated from (9), i. e. from $z = 2\,(1 + \gamma) : r$.

The relation (10) seems, therefore, to hold very accurately. It comes to this that $r - 1 = 2 : z$, or

$$\frac{v_k - b_k}{b_k} = \frac{2\,b_0}{b_k},$$

hence

$$\underline{v_k - b_k = 2\,b_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If, namely, only for ideal substances we find $v_k - b_k = 2\,b_k$, so that then v_k becomes $3\,b_k$ — now this property appears to continue to hold for *all* substances, if only in the second member $2\,b_0$ *is substituted* for $2\,b_k$ (in which b_0 is therefore always the volume v_0 at $T = 0$ extrapolated from the equation of the straight diameter). As therefore

$$\underline{\frac{v_k}{b_0} - \frac{b_k}{b_0} = 2} \text{ or } \underline{s' - z = 2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11a)$$

and as $v_k : b_0 = 2\,(1 + \gamma)$ according to (9), we also have simply:

$$\underline{z = \frac{b_k}{b_0} = 2\,\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

And this is what the new-found relation really comes to. In this way we have for

Ordinary substance	$\gamma = 0{,}9$	$z = 1{,}8$
Argon	$\gamma = 0{,}75$	$z = 1{,}5$
Ideal substance	$\gamma = 0{,}5$	$z = 1$

For an ideal substance we take $\gamma = 0{,}5$, because there just as for the other substances the coefficient of direction has been taken of the straight line which connects the critical point with the point d_0 at $m = 0$. The always slightly deviating direction of the locus $\frac{1}{2}\,(d_1 + d_2) = f\,(m)$ *close to* the critical point would be $= 0{,}4$. (Compare my earlier papers of 22 Nov. 1911, p. 438 et seq., of 24 Jan. 1912, p. 563 et seq. and 574, and of 25 April 1912, p. 1091 1096). That the so-called "straight diameter" really exhibits a slight curvature at the last moment in the immediate neighbourhood of the critical point, has been found among others by CARDOSO for different substances.

From the above a remarkable relation can still be derived, namely, $s' - 2$ being $= z$ according to (11a), and z being $\frac{2}{r-1}$ according to (10):

$$s' - 2 = \frac{2}{r-1} \, ,$$

or as $r-1$ is always $= s : (f' - s)$ according to (a):

$$s' - 2 = 2\frac{f' - s}{s} \, ,$$

from which immediately follows:

$$\underline{2f' = ss'} \quad \ldots \ldots \ldots \quad (13)$$

Thus e.g.

Ordinary substance	$s = 3{,}77$	$s' = 3{,}8$	$f' = 7{,}16$
Argon	3,424	3,5	5,99
Ideal substance	2,667	3	4

Here attention must once more be drawn to the difference between $s = RT_k : p_k v_k$ and $s' = v_k : v_0$, which difference is, indeed, small, but never negligible. Thus for an ideal substance $s' : s = {}^9/_8$. The empirical equalisation of s' and s would only lead to *approximate* relations (v. D. W.), whereas our above empirical relations are perfectly exact, and seem to hold accurately for all substances.

6. The found relation between z and r (in (10)), and in connection with (9) therefore also between r and γ — which relation will have to be *theoretically* justified *by the course of the function* $b = f(v)$, through which $b_k : b_0$ becomes $= 2\gamma$ according to (12), which will be discussed presently — now enables us in connection with the assumption $\lambda_1 : \lambda_2 = 1$, to express *all* the quantities relating to the equation of state in the one independent parameter γ.

In the first place we choose γ, because this quantity according to (12) is in the closest relation with the course of the function $b = f(v)$, on which after all everything is founded: all the difference between the great diversity of the substances. But in the second place because this quantity γ, as said, can be easily experimentally determined, as for this purpose only a number of liquid- and vapour densities must be determined not up to the critical temperature, but near to it.

From (9) and (10) follows with regard to r:

$$z = \frac{2(1+\gamma)}{r} = \frac{2}{r-1} \, ,$$

hence

$$r=\frac{1+\gamma}{\gamma}\quad\ldots\ldots\ldots\ldots\quad(14)$$

Then from (3), viz. $rs=8\times(\lambda_1:\lambda_2)$, when $\lambda_1:\lambda_2=1$ is put,

$$s=\frac{8\gamma}{1+\gamma}\quad\ldots\ldots\ldots\ldots\quad(15)$$

follows for s, whereas from $s'=2\,(1+\gamma)$, (see (9)), follows:

$$\frac{s'}{s}=\frac{(1+\gamma)^2}{4\gamma}\quad\ldots\ldots\ldots\ldots\quad(16)$$

From $f'=8s:(8-s)$ (see a little above (7)), or also from $f'=\frac{8}{r-1}$ according to (4) we derive:

$$\underline{f'=8\gamma,}\quad\ldots\ldots\ldots\ldots\quad(17)$$

an exceedingly simple relation, which states *that the critical coefficient of pressure* f' 1) *will always be equal to eight times the reduced coefficient of direction of the straight diameter.*

From (7) follows for γ:

$$\lambda=\frac{27\,\gamma^2}{(1+\gamma)^2(8\gamma-1)}\quad\ldots\ldots\ldots\quad(18)$$

Further according to (7) we have:

$$1-b'_k=\frac{8\gamma-1}{4\gamma(1+\gamma)}\,;\quad b'_k=\frac{(2\gamma-1)^2}{4\gamma(1+\gamma)}\,;\quad \frac{b'_k}{1-b'_k}=\frac{(2\gamma-1)^2}{8\gamma-1}\ .\quad(19)$$

Then also according to (7):

$$-\beta''_k=-\frac{v_kb''_k}{1-b'_k}=\frac{f'-4}{f'}=\frac{2\gamma-1}{2\gamma}\quad\ldots\ldots\quad(20)$$

Thus we arrive, substituting $b_k:b_0$ for 2γ according to (12), at the exceedingly simple relations at the critical point:

$$\underline{b'_k=\frac{(b_k-b_0)^2}{b_kv_k}}\,;\quad \underline{-\beta''_k=\frac{b_k-b_0}{b_k}}\quad\ldots\ldots\quad(21)$$

From this we can already get an insight into the probable values of b' and β'' also outside the critical point, and try to derive the relation $b=f(v)$ by integration. But this will be discussed later.

If we now finally summarize what has been found, in a table in which some principal types of known substances have been inserted, we get the following instructive summary, from which it may be seen how the *whole* behaviour of the substance can be deduced from one fundamental quantity — here the quantity γ (also $={}^1/_2\,(b_k:b_0)$), the reduced coefficient of direction of the straight diameter according to ${}^1/_2\,(d_1+d_2)-1=\gamma\,(1-m)$. We may further avail ourselves of the following table for the *prediction* of still un-

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1) In which f' is properly speaking $=f:(1+\varphi)$, see (5). But f' always differs exceedingly little from f.

known values (for helium and hydrogen e.g.) or for the *correction* of already determined values (among others for oxygen).

	γ	$z=\frac{b_k}{b_0}$	$\mathbf{r}=\frac{v_k}{b_k}$	$s'=\frac{v_k}{v_0}$	**s**	$s':s$	$\mathbf{f}'$	λ	b'_k	$-\beta''_k$
Limiting substance[1])	**1**	2	**2**	4	**4**	1	**8**	0.964	0.125	0.55
Ordinary substances[2])	0.9	1.8	2.11	3.8	3.79	1.003	7.2	0.977	0.0936	0.444
	0.8	1.6	2.25	3.6	3.55	1.0125	6.4	0.988	0.0625	0.375
oxygen Argon	0.75	1.5	2.33	3.5	3.43	1.02	6	0.992	0.0476	0.333
Hydrogen Helium	0.6	1.2	2.67	3.2	3	1.067	4.8	0.999	0.0104	0.167
Ideal substance	0.5	1	3	3	2.67	1.125	4	1	0	0

Now for H_2 has been found $s = \pm 2{,}9$, $f = 4{,}83$; so this agrees very well with our type, where $\gamma = 0{,}6$ ($s = 3$, $f' = 4{,}8$). Accordingly we may expect for H_2 a straight diameter, the reduced coefficient of direction of which will amount to 0,6.

For helium has been found $s = 3{,}13$, $f > 4{,}46$; this too may be correct. If s is really 3,13, f would even be greater than 5. But if f is no more than 4,5, then γ would be $= 0{,}56$, and $s = 2{,}9$, just as for H_2.

And, at last, for O_2 has been found $s = 3{,}346$, $f = 5{,}76$, $\gamma = 0{,}813$, where the values of s and f are in good harmony, but γ deviates greatly. For with $f = 5{,}76$ would correspond $\gamma = 0{,}72$, $s = 3{,}349$, so that s as has been said, agrees beautifully, but γ ought to be considerably lower than 0,813. But here the fact may also have influence that liquid oxygen is an *associated* liquid, and that hence (just as for ethyl and methylalcohol, acetic acid, etc.) γ is *higher* than the normal value.

7. We will not drop this subject before having set forth a few points. First: the circumstance, to which putting $\lambda_1 : \lambda_2 = 1$ really comes, is this. According to (γ) $\lambda_1 : \lambda_2 = s : 8\,(1 - {}^{s}/_{f'})$ and so when $\lambda_1 = \lambda_2$ is assumed, this comes to this that $s = 8f' : (8 + f')$ (see above (7)). This is experimentally satisfied. But further $f' = 8\gamma$ — also in consequence of the new relation (12) — and according to (21) $b'_k = (b_k - b_0)^2 : b_k v_k$. The latter is in connection with the form

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[1]) Substance with high molecular weight.

[2]) Mean of *n*-pentane, *i*-pentane, fluorbenzene, etc.

of the function $b = f(v)$, and so the particular form of this last function is after all the deeper cause that both $\lambda_1 = \lambda_2$, and the new relations found by me, viz. $v_k - b_k = 2b_0$ and $b_k : b_0 = 2\gamma$ are satisfied.

I further draw attention to the fact that the above relations only remain valid as long as the law of equipartition continues to hold at very low temperatures. I have convinced myself for argon that the departures from this law even at the lowest temperatures, at which vapour-pressure determinations etc. have still been made below the critical temperature — among others at 90° K. — are still so slight that they remain entirely below the errors of observation. But this will be treated more fully in a following communication. Whether this is the case at the critical temperatures of hydrogen and helium, I have not yet examined. It is, however, very well possible that for such exceedingly low absolute temperatures the deviations are large enough to give rise to more or less considerable deviations in the formulae. This can particularly affect the quantity γ, as the straight diameter extends to still lower temperatures than the critical temperatures.

Finally a few remarks on the way in which b depends on the temperature. It has appeared to me that this variability is exceedingly slight at higher temperatures, so that even at the critical temperature of *ordinary* substances $\frac{\partial b}{\partial T}$ is still negligible (See § 1 and 2). This is in agreement with what I found before for H_2[1]. For 0°, 100°, and 200° C. I found, namely, b_g constant $= 917 \times 10^{-6}$ (p. 576, 580 and 582 loc. cit.). But b_0 varied greatly. That b_0 varied and even apparently *increased* according to the relation $b_g - b_0 = \sqrt{\gamma T}$ was entirely owing to the form of the chosen function $b = f(v)$, viz. the wellknown "equation of state of the molecule" of VAN DER WAALS.

It has, however, become clear to me that this equation does not hold, and is in contradiction to the above given accurate values b'_k and β'_k. The fact is this that b *decreases* at *all* temperatures, but the more as the temperature is lower. Finally b_g will have become $= b_0$ at the absolute zero; hence no variation of b with the volume will then be possible any more. For at a given temperature b moves between b_g (for $v = \infty$) and b_0 (for $v = v_0$). Now b_g is a temperature function, and it moves from b_∞ (for T large) to b_0 (for $T = 0$). Hence in a b,v-diagram at high temperatures the curve $b = f(v)$ will have a pretty steep inclination from $b_g =$ about 1,9 b_0 (for ordinary substances)

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[1] These Proc. of 24 April 1903, p. 573—589.

to b_0. But at low temperatures this curve will approach the *straight* line $b = b_0$ more and more, moving from b_0 to b_0.

Now as has been said, the decrease of b_g with T is so slow at first that $b_g = b_\infty$ at T very great is not very different from b_g at T_k, when namely T_k is comparatively high, as for all "ordinary" substances. Only at lower temperatures b_g decreases rapidly to b_0. In consequence of this $\frac{\partial b}{\partial T}$ will, therefore, be comparatively very small in the neighbourhood of T_k, but $\frac{\partial^2 b}{\partial T^2}$ will assume a much greater value.

So this accounts for the fact that for substances with *low* critical temperatures, as O_2, Argon, H_2 and Helium the ratio $b_k : b_0$ becomes smaller and smaller (see the table), which will cause the type to *approach more and more* to that of the so-called ideal substance, where VAN DER WAALS' ideal equation of state with constant b will hold. For once more: at lower temperatures b_g approaches b_0 more and more, and the distance between b_g and b_0 disappears.

But that this is not the *only* cause of the change of type, so that e.g. Xenon with a comparatively high critical temperature (+ 16°,6 C.) is identical in its behaviour with O_2, where $T_k = -119$°C. — this is perhaps owing to this that a second circumstance can be of influence on the course of b as function of v, namely that the relation $\frac{v_0}{b_0}$, which will probably depend on the structure of the molecule (compound or simple as for argon, helium etc.), need not always be $= 1$. This too will be discussed later.

Both the varying value of b_g with decrease of temperature, and the variable value of $v_0 : b_0$ according to the nature of the different substances: these are the principal causes of the preservation of the individuality of the great majority of substances also in their *reduced* equation of state, so that these substances may be divided into different classes, ranging from the class of the "limiting substance" with high molecular weight, and of the ordinary substances, to that of the "ideal" substance with extremely low critical temperature, for which would hold $f = 4$, $r = 3$ and $s = {}^8/_3$. But even helium (see the table) is still a long way from this.

In a following paper we shall treat the form of the function $b = f(v)$, and test the found expressions by the values of b which I have calculated for *Argon*.

I will communicate already here, that of the many expressions which satisfy the relations (21), i.e. which at T_k give the values of

b'_k for β''_k indicated there, only some types lead to simple results[1]), among others also (with some restriction, see later on) the exponential type proposed already before by KAMERLINGH ONNES:

$$b = b_g - (b_g - b_0)e^{-\alpha(v-v_0)}.$$

Already in 1901 (Archives Teyler (2) T. VII, Troisième partie) I tested (see p. 14 et seq.) the values of b for H_2 and CO_2 by this equation[2]), and found a good agreement. But that I then found deviations with respect to the critical quantities is simply owing to this that I at the time did not take b_g variable with the temperature, and that therefore observations of H_2 at 0° C. can by no means give a final decision about the quantities at —241° C.

It is of course only of formal importance, when in the above relation and others at last b_g and v_0 are replaced by critical quantities, so that the relations (21) are satisfied. But this will be discussed in a subsequent paper.

Fontanivent sur Clarens, January 1914.

Physics. — *"An apparatus for the determination of gas isotherms up to about* 3000 *Atm."* (*Continuation.*) VAN DER WAALS-fund researches N°. 6. By Prof. PH. KOHNSTAMM and K. W. WALSTRA. (Communicated by Prof. J. D. VAN DER WAALS.)

(Communicated in the meeting of January 31, 1914).

B. *The volume measurement.* (*Continuation*).

CONVEYANCE OF THE GAS INTO THE MEASURING TUBE.

In the previous communication the question was answered how the volume is determined of a quantity of gas which is in the measuring tube, above mercury. Now we shall have to describe how we get the gas quantity that is to be measured, in this position. For this the most intricate part of the apparatus is required.

As is known AMAGAT's measuring tubes consisted of piezometers

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[1]) Also v. d. WAALS' relation in the general form $\frac{b-b_0}{v-b} = f\left[1-\left(\frac{b-b_0}{b_g-b_0}\right)^n\right]$ with b_0 constant gives perfectly impossible results, among others n varying between 8 and 30.

[2]) It is easy to see that the relation used there, viz.

$$b = b_\infty\left(1-\theta e^{-\beta\frac{v}{b_\infty}}\right)$$

by the application of suitable substitutions for θ and β is identical with the above relation.

of the well-known CAILLETET form. The quantity of gas is measured at low pressure, the piezometer is placed in a steel vessel filled for the greater part with mercury and further with a transmission liquid; and by then forcing up this liquid by means of a hydrostatic press we expel the gas from the piezometer reservoir, and convey it to the calibrated stem. Through this way of procedure, however, we are compelled to confine ourselves to a comparatively small quantity of gas. For if we should want to start from e.g. 1 *l.* of gas under normal circumstances, the steel pressure vessel must itself have at least a capacity of 2 *l.* And to construct a vessel of such a capacity, which can be perfectly closed, and does not leak at 3000 atm., is, if feasible, so expensive that its execution is entirely out of the question. Yet it is very desirable not to work with small quantities that the volumes may not become too small at high pressure. To enable us to work with a quantity of gas of 1 *l.* without the parts of the apparatus exposed to high pressures becoming of too large dimensions, an apparatus was constructed which allows us to compress the quantity of gas to be measured first to from 50 to 100 atm., and then convey it to the measuring tube proper.

A first requirement is that throughout the experiment the measuring tube must be continually exposed to the same pressure outside and inside, because else the thin glass tube of course at once gives way. Originally it was the intention to convey the quantity of gas quantitatively into the measuring tube, after its normal volume had been determined. Owing to unforeseen difficulties, to which we shall revert further on, we have not yet succeeded in realizing this quantitative transferrence, so that in the experiments which will be described in what follows, the quantity of gas which was worked with, has been only determined by a measurement of its volume e.g. at 100 atm., the compressibility between 1 and 100 atm. having to appear from separate determinations. We shall discuss this more extensively later on in the description of the experiments, and shall now first proceed to give a description of the apparatus, used for the conveyance of the gas into the measuring tube.

It consists of three pressure stages: an (unprotected) glass part for the pressures below two atmospheres; a part that serves to compress the gas from 2 to 50 or 100 atm.; and the measuring part proper. The glass part consists of a vessel A of a capacity of ± 1 *l.*[1]), placed in a copper thermostat with glass windows (repre-

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[1]) As we have not made use of the accurate capacity of this vessel for the experiments which will first be described, we shall not enter into a description of its calibration as yet.

sented schematically in fig. 6). At its bottom the vessel A passes into a tube B, which is in connection by means of a side tube with a Gaede-airpump and other auxiliary apparatus to be used in the filling. The tube B passes through the bottom of the thermostat, and is connected with a large pear-shaped mercury bulb by means of a rubber tube.

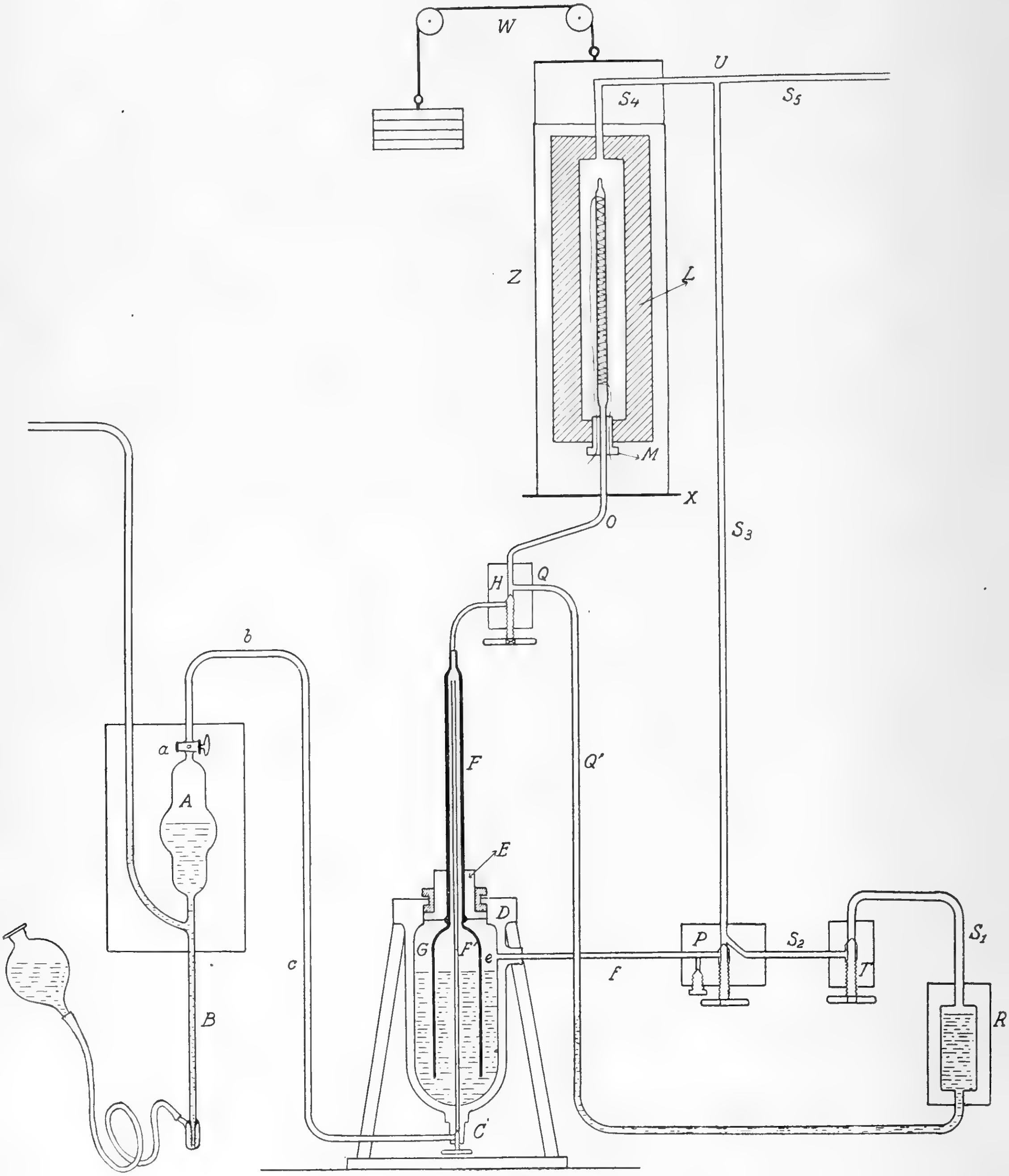

Fig. 6.

At the top of the glass vessel there is a cock *a*, which, opened, gives access to the glass tubing *bc*, which leads to the steel high pressure cock *C*. This cock has been specially constructed for the quantitative transferrence of gases, as was described in these Proceedings already before.[1]

With this cock we reach the second "pressure stage". It consists chiefly of a large cast-iron vessel *D* of more than 2 *l.* capacity, which can be closed at the top with a heavy iron piece *E* with bayonet joint and leather packing. This piece *E* is bored through and a heavy glass tube *F*, of more than barometer height, has been cemented in it. On its bottom this tube *F* is attached to a glass jar *G*, of about 1 *l.* capacity; at its top it passes with a sealing-wax joint into a steel capillary, which gives a connection with the high-pressure-cock *H*, which can shut off the third "pressure stage".

The said cock *C* is fastened to the bottom of the iron vessel *D*; the vertical opening is in connection with a thin glass tube *F'*, of a length of at least 80 cm. When the piece *E* with the glass jar *G* is placed into the iron vessel, the tube *F'* gets inside *F*, as is shown in the figure. Through an aperture *e* the vessel *D* is further in connection with a steel tube *f*, which connects *D* with the high pressure-three-way-cock *P*, where the third pressure stage begins again. The tube *f* is again connected with *D* by means of a steel-to-steel closure, as was already described in this series of communications[2]). On the steel tube *f*, the end-piece of which is ground conical, a double steel cone *g* is screwed, which is in its turn pressed against *D* by means of a flange plate *h* with bolts, fastened in the iron vessel *D'* and nuts. (Cf. fig. 7). The closure of *E* in *D* is elucidated by fig. 7*a* and 7*b*. A steel ring E_2 is pressed into a leather ring E_3, which is *V*-shaped in section by means of a plate E_1 fastened with screws on *E* (see the figure). The leather ring extends through the pressure, presses therefore against *E* and *D*, and effects in this way the closure. *E* is held in its place by a piece D_1 with bayonet joint. When the projecting sectors D_2 are rotated so that they get before the opening D_3 of the rim D_4 (see fig. 7*b*), the piece D_1 can be taken out, and with it the piece *E* and *G*.

The highest pressure stage consists in the first place of the observation vessel proper *L*, a heavy steel tube of ± 1 m. length and

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[1]) These Proc. XI, p. 915.

[2]) These Proc. XV, p. 1024 and fig. 2.

1,65 cm. bore, which is calculated to resist a pressure of 4000 atm and is suspended on the ceiling by means of rods. At the bottom

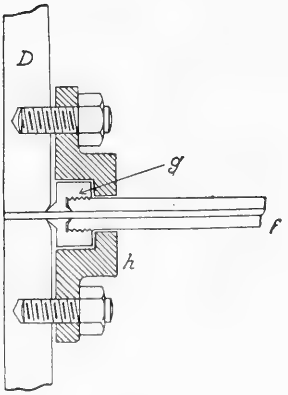

Fig. 7.

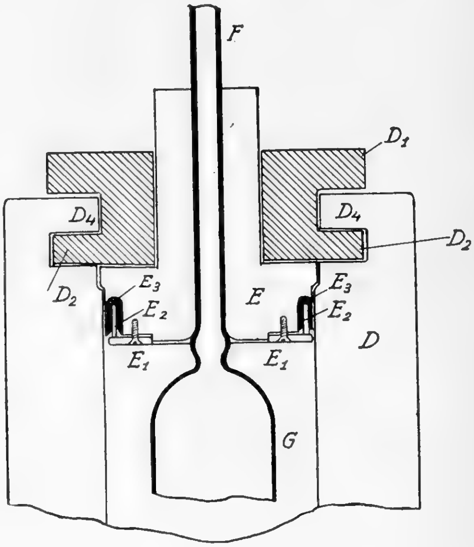

Fig. 7*a*.

L is closed by a shutter piece M, the construction of which we shall discuss presently. M is bored through, and this boring terminates in a steel tube N (fig. 11), to which the glass observation tube is

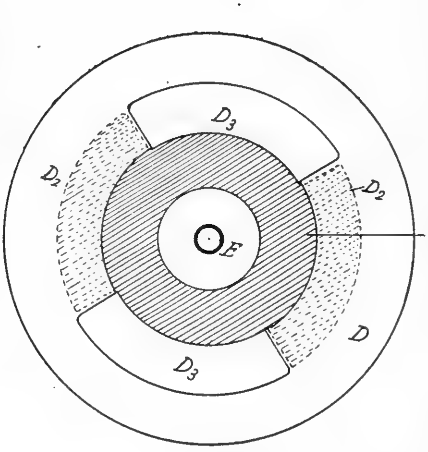

Fig. 7*b*.

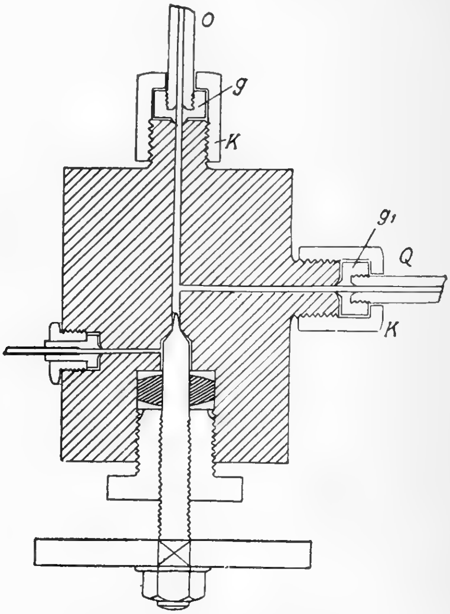

Fig. 8. Cock H.

fastened. The other side of the channel in the shutter piece M is connected through a cone and nut K[1]) with a steel capillary tube O, which leads to the before mentioned cock H. The construction of this cock appears from fig. 8. The tube O always remains in communication with the righthand side opening, which opens again into a steel tube Q', which leads further to the mercury vessel R. By opening or closing the cock H we can, however, bring O in connection with, resp. shut off from the glass jar G in the iron vessel D. The mercury vessel R is by means of a steel tube S_1 in communication with a high pressure cock T, which can effect or prevent the communication with the steel tube S_2. And finally this tube S_2 again leads to the before mentioned high pressure three-way cock P. The construction of this cock appears from fig. 9. The stopper t only serves to shut off an opening, through which at the end of an experiment when one wants to lead back the gas into the jar G, oil can escape. It is seen that S_2 is always in communication with a third tube S_3, but that a communication can be made or broken off of S_3 and S_2 with the tube f and so with the second pressure stage by the opening or the closure of P. S_3 terminates in a T-piece U, which on one side is in communication through the tube S_4 with the upper side of the observation vessel L in entirely the same way as the tube O with the bottom side,

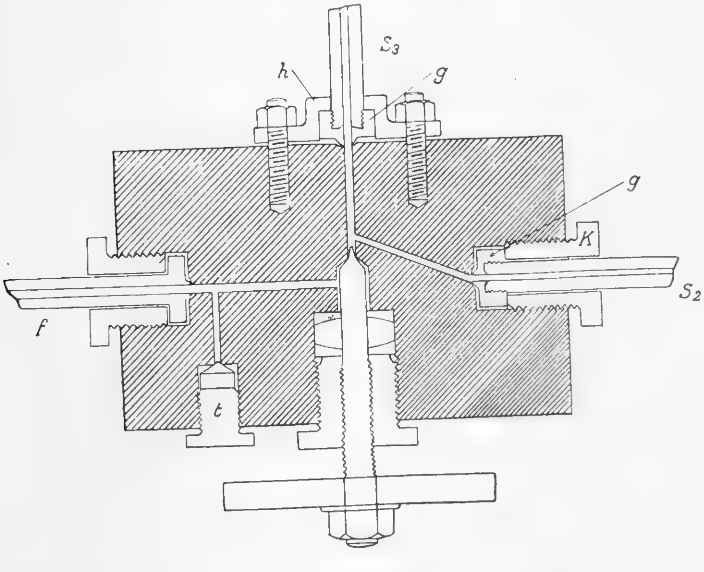

Fig. 9. Cock P.

on the other side through S_5 with the hydrostatic press, which causes the pressure.

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[1]) Cf. the description of these connections lower down.

By the aid of this arrangement it is now possible to fill the measuring tube, which is fastened at *N* on the piece *M* with the gas that is to be measured, this glass tube being always subjected to the same pressure on the inside and on the outside.

After the whole system of tubes and all the cocks etc. have been cleaned, the mercury vessel *R* is filled entirely, and the vessel *D* half with mercury. By the application of a slight pressure the mercury in *Q'* rises, and fills the whole tube *Q* up to the cock *H*. Then the cock *T* is closed, so that the mercury in *Q* cannot move up and down any longer. When this pressure is applied, the vessel *L* outside the glass tube has filled with the oil, which is used as pressure transmission liquid. Now all the cocks except *T* are opened, and the whole system *A abc F' FON* is exhausted by means of the GAEDE-pump. Then the mercury from *D* rises in the jar *G* and reaches barometric height between *F* and *F'*. Now the apparatus may be rinsed once or twice with gas by admitting gas at *B* by means of the mercury reservoir, and then making a vacuum with the GAEDE-pump. If we now want to bring a definite measured quantity of gas into the measuring tube, we close *a*, and admit a quantity of gas into *A*. When the mercury reservoir is then raised, a quantity of gas is isolated in *A*, the pressure, the volume, and the temperature of which can be determined. If now the glass cock *a* is opened, the gas flows into the exhausted space *cF'*. Now the mercury in *F* falls, and by raising the mercury reservoir which is in communication with *B*, we can now expel the gas from *A* to *D*. If we want to do this quantitatively, we must raise the mercury reservoir so much that the mercury overflows at *b*, and fills the whole tube *bc*, and that at last it becomes visible at the upper end of *F*. *C* is then closed. The gas is then under a pressure of about one atmosphere in the jar *D*, and further in *FON* and in the measuring tube.

By the hydrostatic press, resp. through the way $S_5 U S_3$ *Pfe* we now increase the pressure. The mercury in *D* then descends outside the jar *G* and rises inside it, and expels the gas more and more from the jar towards *F*. The pressure in the measuring tube then rises, of course. But *U* being in communication with *L* through S_4, the pressure inside and outside the measuring tube is always the same. If we want to convey quantitatively, the pressure must be raised so high that the gas has been entirely expelled by mercury from *G* and *F*, and the mercury has reached the steel capillary above *F* and finally *H*. Then *H* is closed. Now the communication between the inside and the outside of the measuring tube is broken.

We should, therefore, take care that in this condition no great variations of pressure can take place, which might make the measuring tube burst. This is controlled by a spring manometer, which is in connection with the hydrostatic press. In the operation it appears, however, that a few atmospheres' difference of pressure is not yet dangerous to the measuring tube. The dimensions of the measuring tube must be so chosen in proportion to the jar G that all the gas has been expelled from G and F by mercury before 80 to 100 atm. have been reached, as the unprotected glass tube F cannot resist a higher pressure. Now P is closed. This separates the high pressure division, in which the measurements take place, entirely from the second pressure stage, D etc. For H has already been closed (see above). Now T is opened. This opens again the communication (by the way $S_4\ U\ S_3\ P\ S_2\ TS_1\ RQHO$) between the inside and the outside of the measuring tube. If we now continue to raise the pressure by the hydrostatic press, the mercury rises in H resp. O, and pushes the gas further and further above it, till at last the mercury reaches the tube N and then the measuring tube. Still further increase of pressure then brings the mercury into contact with the platinum contacts in the measuring tube one after another. All through the measuring tube remains constantly exposed to the same pressure on the inside and on the outside. When we want to suspend the measurements temporarily, this continues to be the case. For then a cock in the hydrostatic press is closed which shuts the conduit S_5. The closure of the apparatus is so perfect that when this cock is closed the high pressure stage ($LHRTPU$, and the connecting system of tubes) can be left at a few hundreds of atm.'s pressure for weeks, without a trace of leakage being observed.

This perfect closure is obtained by the application of steel-to-steel closure everywhere. Only in the cock T it is inevitable that liquid under high pressure is in contact with packing material. (In the cocks P and H there is of course also packing material, but this packing material belongs to the second "pressure stage").

All the couplings are again of the system indicated in fig. 7 and 8, of course modified according to circumstances at the different places. Thus the couplings for the cock P are represented by fig. 9. A steel cone g is always found, which is then pressed against the piece with which it is to be connected by a nut K or the flange plate h. In the former case the thread of the screw is left-handed, so that when the nuts K are turned on, the cone is screwed tighter, instead of being unscrewed. This precaution is unnecessary in case of a flange plate (fig. 7 and 9). The flange plate is pressed tight by bolts and nuts.

We must discuss the piece *M*, on which the glass measuring tube is fastened, somewhat more fully. This fastening seemed an insuperable difficulty for a long time. We have said up to now that the pressure inside and outside the measuring tube was the same; this is true, however, only by approximation. For the way $R\ Q\ O\ M\ N$ is filled with mercury, the way $RS_1S_2S_3S_4$ with oil, and the difference of height of the measuring tube and R certainly amounting to 1.5 m., there prevails a pressure inside the measuring tube of about 2 atm. less than outside it. The different kinds of cement which we used to fasten the measuring tube on *N* (CAILLETET cement, with or without shellac, sealing wax, also packing material put between, such as ivory) were always cracked by the pressure, even though sometimes only invisible cracks arose. On account of the excess of pressure outside, oil then entered the tube from the outside, and rendered the measurements impossible by contamination of the mercury.

At last it was resolved to platinize the measuring tube over some centimeters' distance on the bottom side, to coat this with copper, and then to solder it to the copper tube *k* fastened on the steel piece *N* (Fig. 10). Now it seemed that a solution was found, but a new difficulty presented itself. When pressure brought the mercury into the tube, it could come in contact with the tin when it passed the place of soldering, and the amalgam formed contaminated the measuring tube. To prevent this the tube was lengthened at the bottom by a conical piece *l*, which fitted in a conical part of the steel pipe *N*. Though it was tried, besides, to improve this closure with zapon lac, the place of soldering was not yet sufficiently protected. We then drew out the measuring tube some centimeters into a point *m*. When the gas is compressed in the tube, part of it will be enclosed in the small space *n* outside the drawn-out point. We must then for the present give up the thought of a quantitative transferrence of a quantity of gas. Besides, care should always be taken that during the measurement of isotherms the mercury does not get below the drawn-out point *m*, because then the quantity of gas in the measuring tube might change. But that the soldering place now remains separated from the mercury by gas up to high pressures, is at present an indispensable advantage.

In the steel piece *M* there are four passages *p*, and through each of them passes an insulated wire. The passages end at the top in a conical widening. In this fits a conical ivory ring *r*, and in this a copper cone *q*. The wire insulated by the passage is soldered to the bottom side of the cone. The upper side of two of these cones is connected with beginning and end point of the volume wire. Only

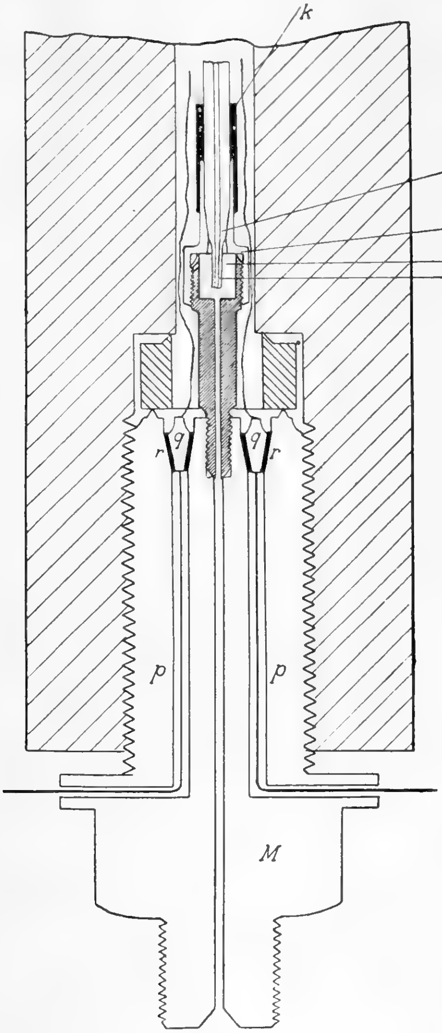


Fig. 10.

the upper side is under pressure, and everything is close fitting on account of the conical form, so that now we have an insulated electrical connection with the measuring tube.

A glass tube closed at the top, on which a platinum wire is wound bifilarly is hung on the measuring tube. The ends of the wire are connected with the two other copper cones.

We shall come back to this in the description of the temperature measurement.

The hydrostatic press.

The pressure is furnished by a **Schäffer** and **Budenberg** hydrostatic press of the known construction, only heavier than usual according to the circumstances. This press is provided with 4 cocks (fig. 11). The tube S_5 is in connection with one of them V_1, and it is this cock that is turned off when in the evening the work is suspended after the measuring tube has been filled with gas. (cf. above p. 829). V_2 can open, resp. break off the communication with the large pressure balance. Here the tube ends, which joins the pump with the "head" A and the space C (fig. 1) of the pressure balance. All the couplings are effected steel to steel as above. V_3 is the exit-valve, V_4 bars the way to the fore pump. This fore pump is an ordinary oil suction- and forcing pump, which can carry the pressure up to 800 atm. So when the whole space beyond V_1 has been filled up to that pressure, V_4 is closed, and the pressure is further increased by means of the large wheel of the press. On the way between V_4 and the fore pump there is still a ⊥-piece. The branch way which is formed here, may be shut off by a high-pressure cock of ordinary construction. This branch

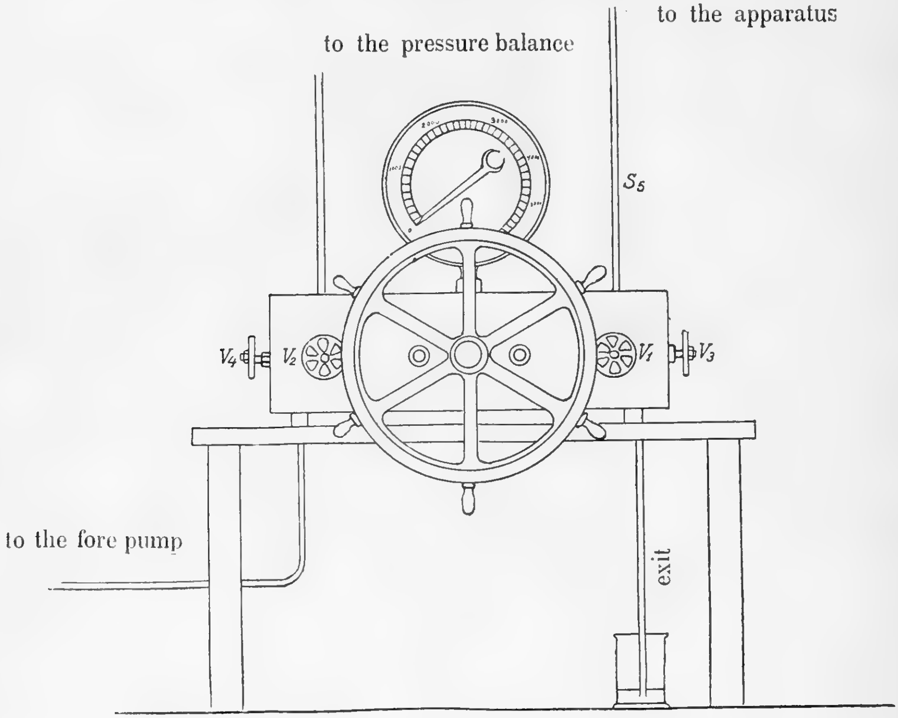


Fig. 11.

way leads on one side to the "head" of the little pressure balance, on the other side to an accurate spring-manometer, which can indicate up to 300 atm. As has been said above, during the time that there is no communication between inside and outside of the measuring tube the pressure is regulated with the aid of this spring manometer.

On the large press stands a large spring manometer of SCHÄFFER and BUDENBERG, which can be used up to 5000 atm.; it serves for a preliminary orientation about the prevailing pressure.

C. *The temperature measurement.*

It was originally the intention to measure the temperature immediately by the side of the measuring tube, so inside the vessel L. The third and fourth insulated wires in the piece M were at first destined for this purpose. But an accurate preliminary investigation, directed to this end, showed that no accurate temperature measurement could thus be attained. For as LISELL and LUSSANA have already demonstrated, the resistance of a metal wire does not only change in consequence of the temperature, but also through the pressure. And this latter variation appeared to be by no means regular. After increase of pressure a wire sometimes returned to its original resistance at atmospheric pressure, sometimes permanent changes of resistance appeared. Besides it would have to be ascertained empirically separately for every wire, how much the change of the resistance with the pressure is, for these changes are by no means equal for wires of seemingly the same material. It is, however, required for such a gauging of the resistance wire that the wire can be placed under different pressures in the pressure apparatus, the temperature being left constant. This can practically not be achieved in another way than by enclosing the whole pressure apparatus in a thermostat, and by taking, under the necessary precautions, the temperature of the thermostat for the temperature of the resistance wire under pressure. But then it is much simpler to apply the same thing directly in the measurements, and assume then too the temperature of the vessel L and its contents to be equal to that of the surrounding thermostat.

A *thermoscope* inside L is, however, indispensable then. In consequence of the compression, resp. dilatation heat of the gas in the measuring tube, namely, variations of temperature of the magnitude of one degree occur inside L. If there is no thermoscope inside L, much time may be needlessly lost in making sure that the stationary state has returned in L. The bifilarly wound wire now, placed on the top of the measuring tube (cf. p. 831) supplies the want of such a thermoscope. This resistance is led outside by the third and fourth insulated wires of the piece M, and brought in connection with a WHEATSTONE bridge. The galvanometer of this combination indicates if the stationary state has set in.

Separate experiments made at atmospheric pressure, so that a resistance thermometer can be put in the space inside L, and moved to and fro, have proved that when the stationary state in L has set in, the same temperature prevails everywhere in L; at least for the temperature at the top and the bottom of L (making use of the thermostat which is to be described presently) no difference of 0°,01 could be demonstrated.

It also appeared that the temperature measured within L and in the thermostat that surrounds L, agreed to within the same amount. This was, however, not the case until not only the whole piece L, but also the closing pieces M, projecting at the top and at the bottom, and a part of the adjoining tubes had been enclosed in the thermostat. In a smaller apparatus constructed first, in which the extremities of L projected outside the thermostat, differences of the order of magnitude of 1° could be demonstrated inside L.

The arrangement of the thermostat can be sketched in a few words. Round L on a steel cable W, which runs over pulleys fastened to the ceiling, hangs a plate-iron cylindre jacket Z balanced by counterpoises; it can be slid up and down a few d. m. On the tube O, which leads from the cock H to M is placed oiltight by by means of a packing box an iron circular plate X, whose section is a little larger than that of the cylindre. At its bottom the cylindre carries a flange, which can be fastened by bolts and nuts on the plate, when the closing piece M and the tube O have been sufficiently screwed tight by means of the nut K belonging to it. A leather packing between flange and plate renders this closure oiltight. The cylindre jacket remains open at the top. An oil pump worked by the repeatedly mentioned transmission shaft then fills the whole thermostat with oil from the large iron store reservoir. By means of a stop-cock fastened in the plate X (not drawn) and a hard lead tubing connected with it, the oil can again be collected in this store reservoir. In a fixed position attached to the cylindre jacket, and therefore moving up and down with it is a stirrer, which when it has been put in its place can again be set going by the transmission shaft. Inside the cylindre a large toluol thermoregulator is suspended, which is in connection with a gas flame which plays against the plate-iron cylindre jacket. By its aid the temperature can be easily kept constant to within 0°.01.

The temperature is determined by a platinum resistance thermometer, which is inserted in a WHEATSTONE bridge formed by a HARTMANN and BRAUN resistance box. The galvanometer is a HARTMANN and BRAUN mirror galvanometer. The image of the incandescent rod of a NERNST-lamp is thrown by a mirror and a lens on a large scale fastened on the wall. The sensitiveness of the instrument is such that a deviation of 0°.01 corresponds with a deviation of about 6 cm. on the scale. So it can be seen all through the room whether the temperature remains constant, resp. how much it changes. The indication of the thermoscope inside L is thrown on this screen in the same way (only the NERNST-burner has here two incandescent rods to distinguish it). Accordingly the observer, who is engaged with the pressure balance or some other part of the apparatus, can ascertain from far whether the stationary state has set in.

The resistance thermometer is gauged with the same leads and in the same bridge arrangement as that with which the measurements take place. For this purpose it is placed by the side of the chief-temperature-normal of the laboratory in a tube filled with oil in the thermostat which surrounds the vessel A; the temperature is here kept constant in the ordinary way.

Amsterdam. *Physical Lab. of the University.*

Botany. — "*Experiments on Hybridisation with Canna indica.*"

By J. A. HONING. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated in the meeting of January 31, 1914).

Among the plants which my Javanese gardener planted in the beginning of 1910 in order to make the empty space round the house look somewhat like a garden, there were two varieties of *Canna*, which occurred as escapes on the high bank of the Deli river. One of them had leaves entirely green, green bracts, a green stem, small red flowers, with yellowish labellum and fruits, which in an unripe condition are green. This variety completely corresponds to the plants, grown from seeds, which I received as *Canna indica* from the Botanic gardens of Buitenzorg. The other had somewhat darker leaves with a red edge and the flowers were also of a somewhat darker red. Further the stem was dark red as were the conical papillae on the unripe fruits.

If Bauer's "Einführung in die experimentelle Vererbungslehre" had at that time already appeared, I should probably have chosen two other forms, differing in more characters, in order to be able to investigate whether there exists a connection between reduction-division and Mendelian segregation, as Bauer considers possible. Since there are only 3 chromosomes in the reproductive-cells of *Canna indica,* only three characters can independently segregate according to Mendel, if the hybrid-segregation is based on the division of the chromosomes of the parents.

The chance that two varieties, which only differ outwardly by the possession and absence of a red colour in almost all their aerial organs, might differ in more than three characters, is at first sight small. Yet this must be the case here, because from the proportions in which the self-pollinated "red" plants segregate as well as from those of the second generation of hybrids it is seen that even for the red edge of the leaves alone the cooperation of three factors is necessary, whilst the colour of the fruits requires at least one additional factor. For this reason the hybridisations have from a theoretical standpoint become of greater importance than I at first suspected.

The *Canna indica* without the red colouring matter has remained constant to the fourth generation. I have had in all 165 specimens, descendants of 14 mother-plants. All are descended from a single "green" *G* 11.

The "red" Canna on sowing was seen to be a hybrid. Only from two specimens, *R* 4 and *R* 13 did I obtain seeds by self-pollination, from most of the others only a little seed after free-pollination. This fact makes it probable that these plants were homozygotically "red", because later I very often got few seeds or none from the pure "red" individuals and a sufficient number from the hybrids. Seeds were obtained after self-pollination from 20 descendants of *R* 4 and from 25 of *R* 13 and although in many cases the proportions, by reason of the small number of specimens, were not wholly certain, yet it was established that segregation occurs in three different ways:

a. In the proportion 3 : 1 (e.g. 27 red and 10 green; 44 red and 15 green; 69 red and 19 green; 24 red and 8 green).

b. In the proportion 9 : 7 (e.g. 146 red and 123 green [theoretically 151.3 red and 117.7 green]; 53 red and 38 green [theoretically 51.2 red and 39.8 green]; 31 red and 24 green [theor. 30.9 and 24.1]; 41 red and 29 green [theor. 39.4 and 30.6]).

c. As 27 : 37 (7 red and 10 green [theor. 7.2 and 9.8]; 11 red and 15 green [theor. 11.0 and 15.0].

These proportions suggest segregation according to three Mendelian factors and this is also completely confirmed by the proportion of the second generation of hybrids. By means of the character of the red leaf-edge the "red" *Canna* can therefore be represented as *AABBCC* and the pure green *G* 11 as *aabbcc*.

Since *R* 4 (9 red and 4 green), *R* 4—1 (27 red and 10 green), *R* 4—1—1 (19 red and 7 green) and also the 4th generation *R* 4—1—1—1 (10 red and 3 green) segregate according to 3 : 1, *R* 4 must, at least if it is assumed that the three factors are independent of one another, be heterozygotic for one of these three and homozygotic for the other two, e.g. *AaBBCC,* which in the following generation gives 1 *AABBCC* : 2 *AaBBCC* : 1 *aaBBCC*. But in that case descendants of *R* 4 must segregate according to 3 : 1 in so far as they are not pure "red" or "green". However *R* 4—1—11 segregated as 9 : 7 (146 red and 123 green) and *R* 4—1—14 likewise (53 red and 38 green). These can therefore be represented for example as *AaBbCC* or *AaBBCc*, because they are clearly heterogyzotic for two factors instead of for one. Since now *AaBbCC* cannot be directly derived from *AaBBCC,* we know that the representation *AaBBCC* for *R* 4 is incorrect and that *R* 4 also must have been heterozygotic for at least two factors, but behaved as if this was so for only one factor and that therefore in their Mendelian behaviour these two factors were not independent of each other.

If we apply this same reasoning to *R* 13—1, which in like manner segregates as 3 : 1 (namely 20 red and 9 green), whilst *R* 13—1—13 separates in the proportion 27 : 37 (7 red and 10 green) then we come to the conclusion that *R* 13—1 must have been heterozygotic for three factors, therefore *Aa Bb Cc,* and nevertheless behaved as a hybrid with only one half-representative factor, in other words, the three factors were not independent but correlated as if there were only the one.

This is established by the second generation of crossing of "pure red" with "pure green". All the specimens of F_1 correspond to the formula *Aa Bb Cc*. Yet segregation took place in *F* 2, as was also the case with the self-pollinated offspring of *R* 4 and *R* 13, not only according to 27 : 37, but also in the proportions 3 : 1 and 9 : 7, as the following table shows.

Probably it is no great error to say when considering all the cases with more "green" than "red" individuals that they segregate in the proportion of 27 red to 37 green, those with slightly more "red" than "green" ones as belonging to those which segregate as 9 : 7 and thirdly, the cases with more than twice as many "red"

TABLE.

Segregation in the second generation of hybrids after crossing of green with pure red-edged specimens.

First generation	Second generation			Agrees with the proportion	Theoretically	
	Number	red	green		red	green
(*G* 11—5)×(*R* 13—4) *R* 1	31	14	17	27 : 37	13.1	17.9
R 3	51	29	22	9 : 7	28.7	22.3
R 4	25	12	13	27 : 37 ?	—	—
(*R* 13—4)×(*G* 11—6) *R* 1	52	28	24	9 : 7	29.25	22.75
R 2	39	21	18	9 : 7	21.9	17.1
(*R* 4—7)×(*G* 11—5) *R* 1	222	95	127	27 : 37	93.6	128.3
R 2	23	10	13	27 : 37	9.7	13.3
R 3	18	8	10	27 : 37 ?	—	—
R 4	195	83	112	27 : 37	82.3	112.7
R 5	58	28	30	27 : 37 ?	24.5	33.5
R 6	62	45	17	3 : 1	46.5	15.5
R 7	77	36	41	27 : 37	32.5	44.5
(R 4-7)×(*R* 4-4 green) *R* 1	18	7	11	27 : 37 ?	—	—
R 3	17	8	9	27 : 37 ?	—	—
R 5	13	9	4	3 : 1 ?	—	—
R 6	16	10	6	9 : 7 ?	—	—
R 7	38	18	20	27 : 37 ?	—	—

as "green" as belonging to the category of those segregative as 3 : 1. When the figures of these three groups are added, the agreement of the totals with the figures is, I think, complete:

Nature of segregation	Found		Calculated	
	red	green	red	green
According to 3 : 1	54	21	56.25	18.75
" 9 : 7	88	70	88.9	69.1
" 27 : 37	319	403	304.6	417.4

Parents which have a hybrid nature for three factors, can therefore distribute these three factors to their off-spring in different ways and in such a manner that the proportional figures show that either all three segregate independently of one another, or that two are correlated and the third remains free or that all three are correlated.

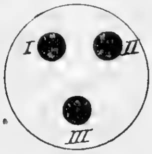
On **Baur**'s hypothesis this phenomenon is easily explained. The factors *A*, *B*, and *C* may be distributed over the three chromosomes as follows:

1. *A*, *B*, and *C* all in 1 chromosome, e.g. in *I*.

2. *A* and *B* together in one chromosome, e.g. in *I* and *C* in another, e.g, *II*.

3. *A*, *B*, and *C* in three different chromosomes e.g. *A* in *I*, *B* in *II*, and *C* in *III*.

By substitution all other possible combinations can be found, which, however, give no other proportional figures than the examples given, which can be represented, as on page 148 of this book **Baur** represents them, e.g. by black for the chromosomes of the "red" plants and white for the "green" ones. The formulae of the reproductive cells appear then as follows:



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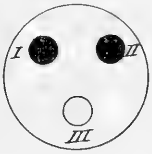

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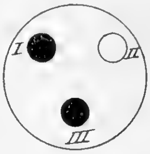

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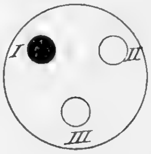

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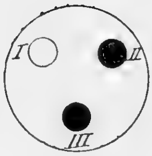

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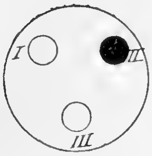

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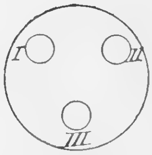

8

Figure	case I	case II	case III
1	*ABC*	*ABC*	*ABC*
2	*ABC*	*ABC*	*ABc*
3	*ABC*	*ABc*	*AbC*
4	*ABC*	*ABc*	*Abc*
5	*abc*	*abC*	*aBC*
6	*abc*	*abC*	*aBc*
7	*abc*	*abc*	*abC*
8	*abc*	*abc*	*abc*
Number of combinations	2	4	8

In the first case there arise only germ-cells of the constitution ABC and abc. With self-pollination therefore segregation of 3 "red" to 1 "green" must follow. In the second case there are four kinds of pollen-grains and four kinds of ova, whereby F_2 will segregate in the proportion of 9 "red" to 7 "green". In the third case there are eight different reproductive cells and segregation takes place in the proportion of 27 "red" to 37 "green".

Baur's hypothetical example of Cannas, which differ in 3 characters, refers to one leaf-, one stem-, and one floral character, which should show independent Mendelian behaviour. We now find that, if we hold to the existing ideas, three leaf characters, which one might perhaps be inclined to assume were in one chromosome, behave, as though they might be distributed over two or three chromosomes, which would be an argument for the dissolution and mixing-up of the chromosomes in the synapsis-stage.

The 17 green examples from $(R\,4—7) \times (G\,11—5)\,R6$ have all been planted out, most of them however died and only 6 grew large enough to ascertain definitely that their leaf-edge completely corresponded with the pure "green" descendants of $G\,11$. They may therefore indeed be represented as *aabbcc*. With respect to the fruits however they differ. Whilst those from $G\,11$ and their offspring possess at most a hardly noticeable red apex on some of the little cones of the fruit wall, the ovaries of one of the "green" examples of $(R\,4—7) \times (G\,11—5)\,R6$ were clearly red, as was the case in some of the examples, which had no red at all in the leaf-margin, from $(R\,4—7) \times (G11—5)\,R_1$. A sister-specimen had, however, green ovaries, so that for the factor red in the fruits the segregation indeed occurs, independently therefore of the three leaf-edge factors, which remain associated.

The great variability of the red in the fruits, even in one and the same plant, is the reason for my failure to determine with certainty the number of factors for it. I can only say that at least one of them can behave as if it were independent of the three leaf-edge factors.

So far the segregation of "red" and "green" has been spoken of as if all "green" individuals were alike. In reality however this is not so. With sowings, not older than 1 to 2 months, no distinction can be made other than that between red-edged and green, because nothing more can then be seen. If however "green" specimens are planted out, then a few months later it is found that some only are wholly green, as $G\,11$, but other specimens show a narrow red edge on the upper half of the leaf, most distinctly at the apex of the young rolled-up leaves. This is the only one of the three factors which becomes separately visible. When it is present heterozygotically, segregation takes place in the proportion of 3 with and 1 without, for example, from *R* 4—2 (green) — 3 I obtained 46 large plants, of which 35 had the narrow red edge and 11 were without it. In the same way out of 35 specimens from *R* 13—1—1 (green) 27 had it and 8 were without it.

In *F*2 of the crosses this segregation is also seen. Of 125 "green" examples of (*R* 4—7) × (*G* 11—5) *R* 1 I obtained only 51 in bloom, the others died by the continuous rain. With segregation in the proportion of 27 : 37 (see the table) 37—16 = 21 plants must occur, which show the narrow red edge, as against 16 real "green" ones. Calculated according to the proportion the number of those with the narrow red edge is 28.94 and of "green" ones 22.05. The figures found were 30 and 21, certainly a sufficient agreement. It is perhaps not unnecessary to add that the 6 specimens which remained from the 16 "green" ones from (*R* 4—7 × (*G* 11—5) *R* 6, were really "green", without the narrow red edge on the leaves.

New crossings of the same two forms but of different origin have in the meantime been made, as also the crossing of *R* 13—4—3 with Canna glauca, which differ in at least ten characters and probably in still more. The whole *F*1 generation is however up to the present only one specimen, of which the fertility is still doubtful. The leaf shape is intermediate between that of the parents; the leaves have still something of the wax-like appearance of the mother and the red edge of the father.

Medan (*Sumatra*), January 1914.

Chemistry. — *"Equilibria in ternary systems." XIII.* By Prof. F. A. H. Schreinemakers.

Now we consider the case, that the substance *F* is one of the components; it is evident that we can deduce then the saturationcurves under their own vapourpressure and the boilingpointcurves in the same way as is done in the previous communications for a ternary and a binary compound.

We take the component *B* as solid substance and now we choose a *T* and *P* in such a way, that no vapour is formed and the isotherm consists only of the saturationcurve *rs* of fig. 1. On decrease of pressure anywhere a gasregion and the region *LG* occur. These regions may arise in different points; in fig. 1 the region *LG*, the liquidcurve of which is indicated by *ed*, may be imagined arisen in *C*. Also two or more of these regions can be formed in different points of the triangle and they can later disappear and come together in different ways.

We may now distinguish several principal cases, according to the appearances in the binary systems *BC* and *BA*.

I. Neither in the binary system *BC* nor in the binary system *BA* the equilibrium liquid—gas shows a point of maximum- or of minimumpressure.

II. In the binary system *BC* or in the binary system *AB* or in both these systems the equilibrium liquid—gas shows a point of maximum- or minimum pressure. We only consider the first case, so that a region *LG* intersects only once as well the side *BC* as the side *BA*. We may distinguish the following cases:

1°. on decrease of pressure or increase of *T* the region *LG* shifts with its liquidline ahead along *CB* from *C* to *B*, and along *AB* from *A* to *B*.

2°. On decrease of pressure or increase of *T* the region *LG* shifts with its liquidcurve ahead along *BC* from *B* to *C*, and along *BA* from *B* to *A*. Consequently the movement is opposite to that sub 1°.

3°. On decrease of pressure or increase of *T* the region *LG* shifts with its liquidcurve ahead firstly along *CB* from *C* to *B*, and after this along *BA* from *B* to *A* or reversally from *A* along *B* to *C*.

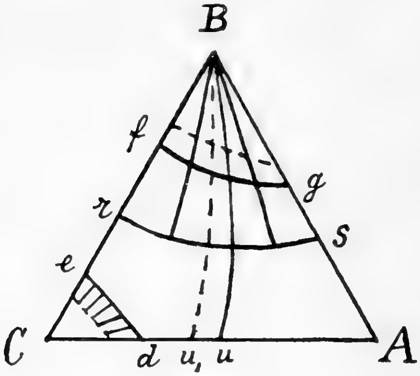

Fig. 1.

In the case mentioned sub 1°. it is to be imagined e.g., that the gasregion arises on decrease of pressure in *C* (fig. 1), expands then across the triangle, and attains at last the point *B*. The one extremity of the region *LG* shifts then on decrease of pressure with its liquid line ahead from *C* to *B*, the other firstly from *C* to *A* and subsequently from *A* to *B*. This case may also be imagined when the gasregion arises in *A* or in a point of *CA* or anywhere within the triangle. This case may yet also be imagined, when different gas regions arise, e.g. in *A* and *C*, which coincide afterwards.

In the case sub 2° it is to be imagined, that the gasregion arises in *B* on decrease of pressure; *fg* (fig. 1) may then represent the liquidcurve of a region LG; the dotted curve situated in the vicinity is the vapourcurve. On decrease of pressure this region LG shifts along BC from B to C and along BA from B to A.

In the case sub 3° we may imagine e. g. that on decrease of pressure the region LG arises in C and disappears in A. On decrease of pressure this region shifts with its liquidcurve ahead along BC from C to B and along CA from C to A. When the one extremity is in B, the other is still somewhere on CA; in fig. 1 Bu is the liquidcurve and Bu_1 is the vapourcurve of a similar region. On further decrease of pressure this region shifts towards point A; as soon as the one extremity has left point B, it obtains of course again a certain breadth.

Let us at first consider the equilibrium $B+L+G$ of the binary system BC. If we represent the quantity of C in the liquid by y and in the vapour by y_1 we have:

$$T\frac{dP}{dT}=\frac{\Delta W_y}{\Delta V_y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

wherein:

$$\frac{\Delta W_y}{T}=H_1-\eta-\frac{y_1}{y}(H-\eta) \text{ en } \Delta Vy=V_1-v-\frac{y_1}{y}(V-v). \quad (2)$$

Under a lower P and at a lower T ΔW_y and ΔV_y are positive. Under a lower P and at a lower T the PT-curve will therefore consist of an ascendant part. The question is whether this curve will show in its subsequent course a point of maximum pressure and a point of maximum temperature.

We shall call, as B is the solid substance, C the solvent. $y_1<y$ means then, that the concentration of the solvent is smaller in the vapour than in the liquid; or also (as $1-y_1>1-y$) that the concentration of the solid substance in the vapour is greater than in the liquid. We shall express this in the following way: the solvent is less volatile than the solid substance. $y_1>y$ means then: the solvent is more volatile than the solid substance. We now distinguish two cases.

$y_1<y$. As $H_1-\eta$ is greater than $H-\eta$ and $V_1-v>V-v$, ΔW_y and ΔV_y can never become zero or negative. Therefore the P,T-curve consists only of a part ascending with the temperature, without a point of maximum pressure or of maximum temperature; it has its highest P and T in the minimum meltingpoint of the solid substance.

$y_1>y$. When $y_1:y$ is greater than 1, this quotient can yet be smaller than $(H_1-\eta):(H-\eta)$, so that in the P,T-curve the point of maximum pressure and of maximum temperature are wanting.

When however $y_1 : y$ becomes greater than $(H_1 - \eta) : (H - \eta)$, while it remains smaller than $(V_1 - v) : (V - v)$, only ΔW_y can become $= 0$ and consequently only a point of maximum pressure occurs.

In order that ΔV_y may also become $= 0$, $V - v > 0$ and as $V_1 - v$ is ordinarily ten thousand times as great as $V - v$, $y_1 : y$ must obtain a very great value. As ΔW_y and ΔV_y may become $= 0$, the P, T-curve has then a point of maximum pressure and of maximum temperature. Therefore we find: the P, T-curve of the binary equilibrium $B + L + G$ is a curve ascending with the temperature, when the solvent is less volatile or only a little more volatile than the solid substance; it may show a point of maximum pressure when the solvent is much more volatile than the solid substance; it may have, besides a point of maximum pressure, also a point of maximum temperature, when the solvent is a thousand times more volatile than the solid substance and this melts with increase of volume.[1]

Let us now consider the saturationcurves under their own vapourpressure of B. For this we take firstly the case sub 1. We now choose the P and T in such a way, that the saturationcurve of B is represented by $r s$ and the liquidcurve of the region $L G$ by $e d$ in fig. 1. On decrease of pressure $e d$ approaches to $r s$. We assume that the first common point arises by the coincidence of r and s. This point is represented in fig. 2 by h. In the same way as for the case that the solid substance is a binary compound we can prove, that $e d$ and $r s$ do not touch one another in h and that although P_h is the highest pressure, under which the system $F + L + G$ occurs, the point h is yet not a point of maximum pressure of the saturationcurve under its own vapourpressure. The vapour corresponding with h is indicated in fig. 2 by h_1.

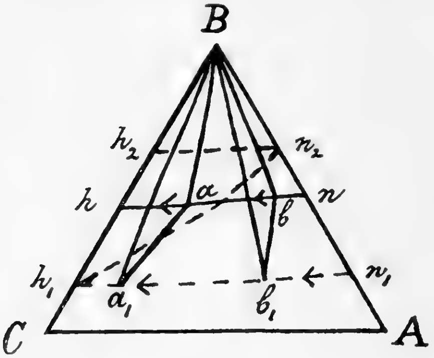

Fig. 2.

Lowering the pressure still more, the intersectingpoint of $e d$ and $r s$ of fig. 1, shifts within the triangle; in fig. 2 a similar intersecting point is represented by a and the corresponding vapourpoint by a_1. From the manner in which the three phase triangle arises, it follows, that this must turn its side solid-gas (Ba_1) towards BC.

When on further decrease of pressure the curves ed and rs of

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[1] See also Ph. Kohnstamm; these communications **15**, (1907).

fig. 1 continue to intersect one another only in one point, under a pressure P_n the points s and d of fig. 1 coincide in a point n of fig. 2; curve $e\,d$ is then situated completely within the sector $B\,r\,s$. Now the saturationcurve under its own vapourpressure is represented in fig. 2 by hn and the corresponding vapourcurve by h_1n_1; the pressure increases in the direction of the arrows, therefore from n towards h. Consequently P_h is the highest and P_n the lowest pressure, under which the equilibrium $F + L + G$ occurs, h not being however a point of maximum- and n a point of minimum pressure of the curve. Further we see, that on change of pressure, the turning of the threephase triangles $B\,a\,a_1$ and $B\,b\,b_1$ is in accordance with the rules formerly deduced.

We have assumed when deducing the above, that the curves ed and rs of fig. 1 intersect one another only in one point under every pressure. It is also possible, however, to imagine that after the formation of the first point of intersection, a second arises by the coincidence of d and s (fig. 1). The liquidcurve of the region LG proceeds then in fig. 1 from s firstly outside and afterwards within the sector Brs. On further decrease of pressure the two points of intersection shift towards one another and coïncide under a pressure P_m in a point m not drawn in the figure; the corresponding vapourpoint m_1 is then situated on a straight line with m and B. The pressure P_m is the lowest pressure under which the equilibrium $B + L + G$ may yet occur; m and m_1 are points of minimum pressure of the curves hn and h_1n_1.

It is evident from the manner in which arises the threephase triangle Bbb_1 in the vicinity of BA that this now must have another position than in fig. 2; its conjugation line solid-gas therefore Bb_1 must be situated between Bb and BA. Two three-phase triangles situated on both sides of the point of minimum pressure turn therefore towards one another their sides solid-liquid.

In the two previous cases we have assumed, that the first common point of ed and rs arises by the coïncidence of e and r. We now assume, that both the curves touch one another in a point M situated within the triangle; the corresponding vapour point M_1 is then situated on a straight line with M and B. The pressure P_M is the lowest pressure under which the equilibrium $B + L + G$ occurs.

On decrease of pressure two points of intersection of ed and rs now arise; the one disappears, when r and e, the other when d and s coïncide. We then obtain again a saturationcurve under its own vapourpressure as hn and a corresponding vapourcurve as h_1n_1 in fig. 2; the points, M and M_1, which are not drawn, are points of maximumpressure. It is evident, that in this case we must imagine in fig. 2 the side Ba of the three phase triangle Baa_1 between Ba_1 and BC.

When we consider in a similar way as above also the cases sub 2° and 3°, we find:

the saturationcurves under their own vapourpressure have a terminating point on BC and one on BA (curve hn in fig. 2). On this curve either a point of maximum or of minimum pressure occurs or there occurs none. The corresponding vapourcurve is situated with respect to hn in the case sub 1° as h_1n_1, in the case sub 2° as h_2n_2 and in the case sub 3° as h_1n_2 (or h_2n_1).

Previously we have seen, that the saturationcurves under their own vapourpressure of a ternary and a binary substance F become exphased at temperatures above the minimum melting point of F. At the deduction of these curves for the binary compound F we have seen, that the point of maximum temperature of the binary system $F+L+G$ takes a prominent position and that these curves occur in the vicinity of this point [point H in fig. 4—6 (XI)]. The same applies also to the saturation curves under their own vapourpressure of the component B; we shall not discuss these here more in detail as similar appearances occur in the case of the boilingpoint curve.

Let us now consider the boilingpoint curves of the component B; firstly we take these curves under pressures lower than the pressure in the minimum meltingpoint of B; we then find: the boilingpoint curves have a terminating point on BC and one on BA (curve hn in fig. 2); on this curve, either a point of maximum- or minimum temperature occurs or there is none. The corresponding vapourcurve is situated with respect to hn, in the case sub 1° as h_1n_1, in the case 2° as h_2n_2 and in the case sub 3° as h_1n_2 (or h_2n_1). If it is desired that in fig. 2 the three phase triangles Baa_1 and Bbb_1 retain their position, the arrows must indicate in opposite direction and the temperature increases, therefore, from h towards n.

It follows from the previous deductions, in what direction the threephase triangles solid-liquid-gas turn on change of pressure (at constant T), or on change of temperature (under constant P). From this also follows the influence of a third substance on the pressure (at constant T) or on the temperature (under constant P) of the binary equilibrium $B+L+G$.

We may also deduce these results in the following way. We represent the quantity of A of a phase by x (or x_1), the quantity of C by y (or y_1), and the quantity of B by $1-x-y$ (or $1-x_1-y_1$). We put, therefore, the origin of our coordinatesystem in the angle point B, the X-axis along the side BA, and the Y-axis along the side BC of the triangle. To the saturationcurve under its own vapourpressure of B then applies:

$$(xr + ys)\,dx + (xs + yt)\,dy = AdP \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$[(x_1 - x)\,r + (y_1 - y)\,s]\,dx + [(x_1 - x)\,s + (y_1 - y)\,t]\,dy = CdP \quad (4)$$

In order to have the boilingpoint curves, we must replace in (3) AdP by $-BdT$ and CdP by $-DdT$.

In the terminating point of both these curves on the side BC, $x = 0$. We then find:

$$\frac{1}{RT}\cdot\left(\frac{dP}{dx}\right)_{x=0} = \frac{\frac{x_1}{x} - \frac{y_1}{y}}{\Delta V_y} \quad \text{and} \quad \frac{1}{RT^2}\cdot\left(\frac{dT}{dx}\right)_{x=0} = \frac{\frac{y_1}{y} - \frac{x_1}{x}}{\Delta W_y}. \quad (5)$$

In the terminating point of both these curves on the side BA, $y = 0$. We then find:

$$\frac{1}{RT}\cdot\left(\frac{dP}{dy}\right)_{y=0} = \frac{\frac{y_1}{y} - \frac{x_1}{x}}{\Delta V_x} \quad \text{and} \quad \frac{1}{RT^2}\cdot\left(\frac{dT}{dy}\right)_{y=0} = \frac{\frac{x_1}{x} - \frac{y_1}{y}}{\Delta W_x}. \quad (6)$$

Herein is:

$$\Delta V_x = V_1 - v - \frac{x_1}{x}(V - v) \qquad \Delta V_y = V_1 - v - \frac{y_1}{y}(V - v).$$

$$\frac{\Delta W_x}{T} = H_1 - \eta - \frac{x_1}{x}(H - \eta) \qquad \frac{\Delta W_y}{T} = H_1 - \eta - \frac{y_1}{y}(H - \eta).$$

From this it is easily found, that the relation 11 (XI) and the rules deduced from this apply also on the addition of a third substance to the binary equilibrium $B + L + G$.

We may in the same way as in the previous communication introduce also in (5) and (6) the perspective concentrations S and S_1 of the new substance. Then S is the part cut off by the line B-liquid, S_1 the part cut off by the line B-vapour from the side CA (fig. 2). When the binary equilibrium $B + L + G$ is situated on BC ($x = 0$), so that A is the new substance, these parts must of course been measured from C; when the binary equilibrium is situated on BA ($y = 0$), so that C is the new substance, they must be measured from A.

When the binary equilibrium $B + L + G$ is situated on the side BC ($x = 0$), we find

$$S = \frac{x}{x+y} \quad \text{and} \quad S_1 = \frac{x_1}{x_1+y_1}$$

Substituting from this the values of y and y_1, in (5), we find:

$$\left.\begin{aligned} \frac{1}{RT} \cdot \left(\frac{dP}{dx}\right)_{x=0} &= \frac{1}{\Delta V_y} \cdot \frac{x_1}{x} \cdot \left(1 - \frac{S}{S_1}\right) \\ \text{and} \quad \frac{1}{RT^2} \cdot \left(\frac{dT}{dx}\right)_{x=0} &= -\frac{1}{\Delta W_y} \cdot \frac{x_1}{x} \left(1 - \frac{S}{S_1}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (7)$$

As S and S_1 are very small we have equated, $(1-S_1):(1-S) = 1$.

When the binary equilibrium $B + L + G$ is situated on the side BA $(y=0)$ we find from (6)

$$\left.\begin{aligned} \frac{1}{RT} \cdot \left(\frac{dP}{dy}\right)_{y=0} &= \frac{1}{\Delta V_x} \cdot \frac{y_1}{y} \left(1 - \frac{S}{S_1}\right) \\ \text{and} \quad \frac{1}{RT^2} \cdot \left(\frac{dT}{dy}\right)_{y=0} &= -\frac{1}{W\Delta_x} \cdot \frac{y_1}{y} \left(1 - \frac{S}{S_1}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (8)$$

We see that (7) and (8) are in accordance with (14) and (15) (XI); we may deduce from this for the addition of a new substance to the binary equilibrium $B + L + G$ the same rules as was done in communication XI for the equilibrium $F + L + G$. It is however to be considered with this that now S and S_1 are positive. We see that the position of the threephase triangles in fig. 2 is in accordance with these rules.

In communication XII we have deduced in different ways form and position of the saturationcurves under their own vapourpressure in the vicinity of the point of maximum temperature and of the boilingpoint curves in the vicinity of the point of maximum pressure of the binary equilibrium $F + L + G$.

All this applies also when the solid substance is one of the components. We must keep in mind that in the binary system $B + L + G$ there occurs not always a maximum of pressure and temperature, which is indeed the case in the binary system $F + L + G$. For that reason we shall express these rules now in the following way.

Let in fig. 5 and 6 (XI) H be a point of maximum temperature of the binary equilibrium $B + L + G$. The saturationcurve under its own vapourpressure of B disappears on increase of T in H [fig. 5 (XI)], when the concentration of the new substance in the liquid is greater than in the vapour; it does not disappear in H [fig. 6 (XI)], when the concentration of the new substance is smaller in the liquid than in the vapour.

If we imagine in fig. 5 and 6 (XI) H to be replaced by the point of maximum pressure Q of the equilibrium $B + L + G$ and the arrows in opposite direction, then we have: on increase of P the boilingpoint curve disappears in Q [fig. 5 (XI)], when the concentration of the new substance is greater in the liquid than in the vapour; it does not disappear in Q [fig. 6 (XI)], when the concentration of the new substance is smaller in the liquid than in the vapour.

Of course we have meant above with concentration the perspective concentration.

From the meaning of the perspective concentrations S and S_1 of a new substance, it follows immediately:

for equilibria in the vicinity of the side BC $(x = 0)$:
when $S > S_1$ then also $y_1 : y > x_1 : x$ and reversally,
when $S < S_1$,, ,, $y_1 : y < x_1 : x$,, ,,
for equilibria in the vicinity of the side BA $(y = 0)$:
when $S > S_1$ then also $x_1 : x > y_1 : y$ and reversally,
when $S < S_1$,, ,, $x_1 : x > y_1 : y$,, ,,

On increase of pressure the boilingpointcurve hn of fig. 2 changes its position and form in order to disappear at last. This may take place in different ways which we shall consider now. We have seen at the deduction of the boilingpointcurves of the binary compound F, that the point of maximum pressure Q of the binary system $F + L + G$ takes a prominent position, it is evident that this is also the case with the boilingpoint curves of the substance B.

We saw before that we may distinguish the three cases mentioned sub 1°, 2°, and 3° with regard to the movement of the region LG on decrease of P or increase of T. In the case mentioned sub 1° as well the solvent C as A is more volatile than the solid substance B. Therefore a point of maximum pressure of the binary equilibrium $B + L + G$ can be situated either on BC or not; the same applies to the side BA.

In the case sub 2° both the solvents A and C are less volatile than the substance B; therefore neither on BA nor on BC can a point of maximum pressure be situated.

In the case mentioned sub 3° C is more volatile, A however less volatile than the substance B; therefore on BC either a point of maximum pressure occurs or it does not; this is however not possible on BA.

With regard to the occurrence of a point of maximum pressure in both the binary systems $B + L + G$, we may, therefore, distinguish three cases:

a. no point of maximum pressure occurs.
b. one ,, ,, ,, ,, ,,
c. two points ,, ,, ,, occur.

In the case sub a the pressure of the binary equilibrium $B+L+G$ increases from C along CB and from A along AB up to B (fig. 2). On increase of pressure the points h and n shift therefore towards B; under P_B (the pressure of the minimum meltingpoint of B) the boilingpointcurve disappears in B.

In the case sub b one of the binary equilibria $B+L+G$ has a maximum pressure, represented in fig. 3 by the point Q. Consequently the pressure increases from C along BC up to Q and from A firstly along AB and afterwards along BC up to Q. Under pressures lower than P_B the boilingpointcurves have therefore one extremity on AB and one on BC between C and Q; under pressures between P_B and P_Q the one terminating point is situated on BQ and the other on CQ.

In the vicinity of the point Q the boilingpointcurves may have two kinds of form. In fig. 3 we have assumed that they disappear in Q on increase of pressure. In the other case, which the reader may draw easily himself, there is one touching the side BC in Q and they disappear in a point within the triangle. A part of these curves has then necessarily a point of maximum- and one of minimum temperature.

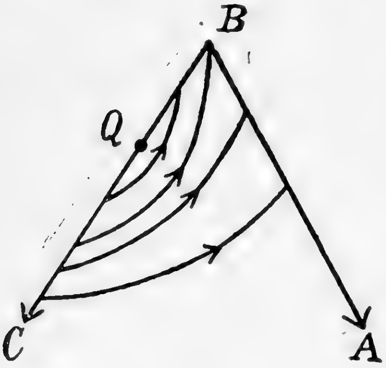

Fig. 3.

From the position of the boiling point curves in the vicinity of the point Q it follows that $S > S_1$ and therefore also $y_1 : y > x_1 : x$ is assumed or in words: if we add to the binary equilibrium $B+L+G$ situated on the side BC $(x = o)$ the substance A, its perspective concentration is greater in the liquid than in the vapour. If we consider that ΔW_y is positive between Q and C, and negative between Q and W, then it follows from (5) or (7), that on the boiling point curves in the vicinity of Q the temperature must increase in the direction of the arrows.

In the case sub c both the binary equilibria $B+L+G$ have a point of maximum pressure, represented in fig. 4—6 by the points Q and Q'. We distinguish three types:

1. in the vicinity of the one point of maximum pressure [Q fig. 4] $S > S_1$; in the vicinity of the other [Q' fig 4] $S < S_1$.
2. in the vicinity of both the points Q and Q', $S < S_1$ (fig. 5).
3. in the vicinity of both the points Q and Q' $S > S_1$ (fig. 6).

In each of these diagrams the pressure increases therefore along BC from B and C to Q and along BA from B and A to Q'

Under pressures lower than P_B, the boiling point curve consists therefore of one single branch with the one extremity on CQ and the other on AQ'; on this curve either a point of maximum (fig. 6) or a point of minimum temperature (fig. 5) occurs or neither of these points (fig. 4).

Under the pressure P_B now also the point B itself occurs, P_B is viz. the pressure of the minimum melting point or in this case as B is one of the components, therefore also the pressure in the triplepoint of the substance B; under this pressure exists the unary equilibrium solid $B +$ liquid $B +$ vapour B. Consequently the boilingpointcurve of the pressure P_B consists of a branch with

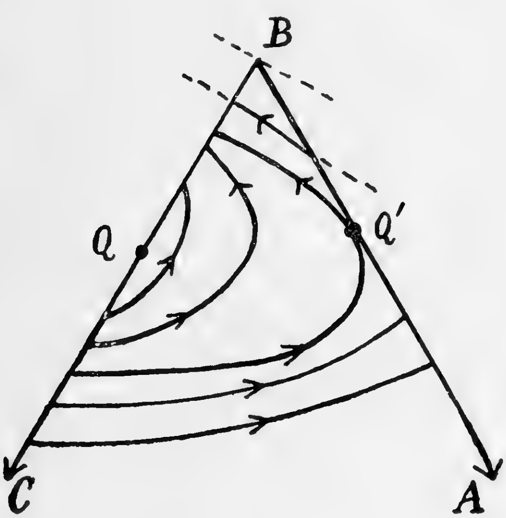

Fig. 4.

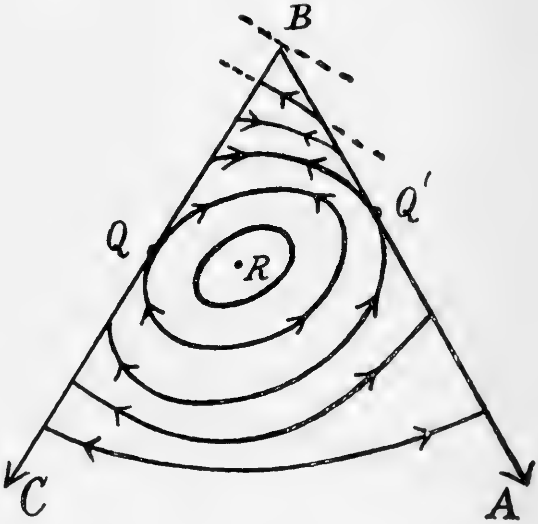

Fig. 5.

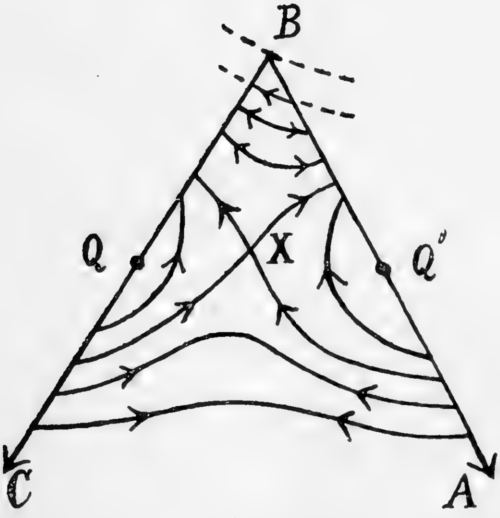

Fig. 6.

the one extremity on CQ and the other on AQ' and of the isolated point B (fig. 4—6).

On further increase of P boilingpointcurves now arise, consisting of two branches separated from one another. In the vicinity of B a new branch is viz. formed with the one end on BQ and the other on BQ' (fig. 4—6). On further increase of P both the branches shift towards one another and under a definite pressure P_X both the branches come together in a point X. This point X is situated 1°. on one of the sides BA or BC, 2°. within the triangle; in the first case X coincides with Q or Q'. In fig. 4 and 5 the two branches come together in Q', in fig. 6 in a point X within the triangle.

In fig. 4 and 5 the boilingpointcurve of the pressure P_Q forms, therefore, a single branch. From our previous considerations it follows that this is curved as a parabola in Q' and touches the side BA in this point. The temperature must increase in the direction of the arrows along this curve in the vicinity of Q'.

On further increase of pressure the boilingpointcurve shifts from point Q' (fig. 4 and 5) into the triangle and we may distinguish two cases. Either it disappears in the point Q on the side BC (fig. 4) or it touches the side BC in the point Q (fig. 5). In the latter case it shifts on further increase of pressure from the point Q into the triangle, so that a closed curve arises, which disappears in R somewhere within the triangle.

In fig. 6 the point X in which the two branches of the boilingpointcurve come together, is situated within the triangle. Here we have a case as was treated formerly in communication X (fig. 5). On further increase of pressure again two branches are formed, separated from one another, which are situated now quite different than at first and on which the points of maximumpressure are wanting. On further increase of pressure the one disappears in Q and the other in Q'.

Besides the diagrams drawn in figs. 4-6, several others may be imagined. For instance we may assume that the two branches of the boilingpointcurve do not disappear in Q and Q' as in fig. 6, but that they touch in these points the sides of the triangle. The boilingpointcurves then consist of two branches separated from one another, which are both closed, and of which the one disappears in a point between Q and X and the other in a point between Q' and X.

We may consider now more in detail the boilingpointcurves in the vicinity of the point B; as in this point x becomes $=0$ and $y=0$, we put:

$Z = U + RT\,(x \log x + y \log y)$ and $Z_1 = U_1 + RT\,(x_1 \log x_1 + y_1 \log y_1)$

We then find for the equilibrium $B + L + G$ in the vicinity of the point B when we put $x = \xi$ $x_1 = \xi_1$ $y = \eta$ $y_1 = \eta_1$ $P = P_B + dP$ and $T = T_B + dT$:

$$\left.\begin{array}{c} \xi_1 = K\xi \quad \eta_1 = K_1\,\eta \\ RT\xi + RT\eta - (V - v)\,dP + (H - \eta_b)\,dT = 0 \\ RT\xi_1 + RT\eta_1 - (V_1 - v)\,dP + (H_1 - \eta_b)\,dT = 0 \end{array}\right\} \quad . \quad (9)$$

Herein, in order to distinguish the coordinate η, the entropy of the solid substance B is represented by η_b.

In order to examine the influence of the pressure on the position of the boilingpointcurves, we eliminate from (9) dT. We then obtain:

$$\xi \Delta W_x + \eta \Delta W_y = -\frac{BC - AD}{R}\,dP \quad . \quad . \quad . \quad . \quad (10)$$

wherein $BC - AD > 0$. (See Comm. II).

When we put in (10) $dP = 0$, we obtain:

$$\xi \Delta W_x + \eta \Delta W_y = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the boilingpointcurve going through the point B.

At first we take ΔW_x and ΔW_y negative, so that the case treated sub c occurs (fig. 4—6). From (11) it follows that ξ and η have the opposite sign; the boilingpointcurve of the pressure P_B is situated, therefore, excepted in the point B itself, completely outside the triangle.

In figs 4—6 a similar curve going through the point B is dotted and a curve situated in the vicinity of B is extended outside the triangle; these parts situated outside the triangle have of course no meaning for us. The direction of the boilingpointcurve going through the point B, is fixed by ΔW_x and ΔW_y; if accidentally $\frac{x_1}{x} = \frac{y_1}{y}$, therefore, also $\Delta W_x = \Delta W_y$, then this curve runs parallel to AC.

We now take a pressure somewhat higher than P_B, therefore dP positive; the second term of (10) is, therefore, negative. From this it follows that the curve cuts off a positive part η from the Y-axis (BC) and a positive part ξ from the X-axis (BA), the curve is situated, therefore, partly within the triangle as in figs 4—6 the curve in the vicinity of B, partly drawn and partly dotted. In accordance with what was treated sub c (figs. 4—6) we find, therefore, that the boilingpoint curve shifts on increase of P from the point B into the triangle.

In the same way it is apparent from (10) that under a pressure, somewhat lower than P_B, therefore for dP negative, the curve cuts off a negative part η from the Y-axis and also a negative part ξ from the X-axis. The boilingpointcurve is, therefore, situated completely outside the triangle. Considering only the stable parts, therefore the parts of these curves situated within the triangle, we can say:

On decrease of P the boilingpointcurve disappears in B;

On increase of P it arises in B and shifts from this point into the triangle.

The direction of the boilingpointcurve in the vicinity of B is determined according to (10) by ΔW_x and ΔW_y. If we put $\frac{y_1}{y} > \frac{x_1}{x}$ then it follows in absolute value $\Delta W_y > \Delta W_x$. If we call the part, which the curve cuts off from the X-axis (BA) ξ_0 and the part which it cuts off from the Y-axis (BC) η_0, then follows from (10) $\xi_0 > \eta_0$.

$\frac{y_1}{y}$ is the ratio of the quantity of C in the vapour and in the liquid, when we add a little C to the unary system solid B + liquid B + vapour B; we shall call this ratio the limit-ratio of C in the equilibrium solid B + liquid B + vapour B. The same applies to $\frac{x_1}{x}$ on addition of A. We may now express what precedes in such a way: when in the equilibrium solid B + liquid B + vapour B the limit ratio of C is greater than that of A, the boilingpointcurve cuts off a smaller part from the side BC than from the side BA.

The above-mentioned rule applies only when ΔW_x and ΔW_y are both negative, therefore, when the P,T-curve of each of the two binary systems $B + L + G$ proceeds from B towards higher pressures.

In figs. 4—6 in B is assumed $\frac{y_1}{y} > \frac{x_1}{x}$ in accordance with this the boilingpointcurve, situated in the vicinity of B cuts off from BC a smaller part than from BA.

When we take ΔW_x and ΔW_y positive, we have the case sub *a*. From (10) and (11) it follows that the boilingpointcurves in the vicinity of B have the same position as in the case sub *c*; on change of P they move, however, in opposite direction. On decrease of P they shift viz. from B into the triangle and on increase of P they disappear in B.

When we take also here $\frac{y_1}{y} > \frac{x_1}{x}$, it follows that $\Delta W_y < \Delta W_x$; we now find: when in the equilibrium solid B + liquid B + vapour B the limit-ratio of C is greater than that of A, the boilingpointcurve cuts off a greater part from the side BC than from the side BA.

In the end $\triangle W_x$ and $\triangle W_y$ may have an opposite sign, so that the case sub b occurs. That there may be accordance with fig. 3, we take $\triangle W_x > 0$ and $\triangle W_y < 0$. From (11) it now follows that ξ and η have the same sign, so that the boilingpointcurve going through B must be situated within the triangle. We see that this is in accordance with fig. 3.

If the pressure is a little raised, so that dP is positive, it follows from (10) that the boilingpointcurve cuts off a positive part η from the Y-axis (BC) and a negative part ξ from the X-axis (BA). If the pressure is lowered, so that dP is negative, then we find that the curve cuts off a negative part η from the Y-axis (BC) and a positive part ξ from the X-axis (BA). If we imagine in fig. 3 some boilingpointcurves still to be drawn in the vicinity of that going through B and these extended outside the triangle as the sides AB and CB, then we see that all this is in accordance with the previous results. Considering only the parts of the curves, situated within the triangle, it follows: the terminatingpoint of the boilingpointcurve going through the point B shifts on decrease of P from B on the side BA and on increase of P from B on the side BC.

Now we shall still examine how the temperature changes along a boilingpointcurve in the vicinity of the point B. For this we choose a boilingpointcurve of a definite pressure $P_B + dP$, so that we must assign a definite constant value to dP in (9). We then find:

$$\triangle W_y \,.\, dT = RT^2 \left(\frac{y_1}{y} - \frac{x_1}{x}\right) \xi + T \,.\, \triangle V_y \,.\, dP \quad . \quad . \quad (12)$$

$$\triangle W_x \,.\, dT = RT^2 \left(\frac{x_1}{x} - \frac{y_1}{y}\right) \eta + T \,.\, \triangle V_x \,.\, dP \quad . \quad . \quad (13)$$

As in (9) the temperature is put equal to $T_B + dT$, dT is, therefore calculated from the point B. Desiring to proceed from the terminatingpoint of the boilingpointcurve on the Y-axis (BC), we put $dT = dT'_y + dT_y$; herein dT'_y is the change of T, wanted to come from the point B in the terminatingpoint of the boilingpointcurve on the Y-axis and dT the change of temperature from this terminatingpoint along the curve. We now have: $\triangle W_y \,.\, dT'_y = T \,.\, \triangle V_y \,.\, dP$. Substituting in (12) $dT = dT'_y + dT_y$, we obtain:

$$\triangle W_y \,.\, dT_y = RT^2 \left(\frac{y_1}{y} - \frac{x_1}{x}\right) \xi \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

When we represent the change of temperature along the boilingpointcurve from its terminatingpoint on the X-axis (BA) by dT_x, we find from (13):

$$\triangle W_x \,.\, dT_x = RT^2 \left(\frac{x_1}{x} - \frac{y_1}{y}\right) \eta \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

Let us firstly consider fig. 3, in the vicinity of the point B of this figure is $\triangle W_y < 0$ and $\triangle W_x > 0$, therefore $\frac{y_1}{y} > \frac{x_1}{x}$. From (14) and (15) it now follows that dT_y and dT_x are both negative. This means that on a boilingpointcurve, situated in the vicinity of B, the temperature decreases from the terminatingpoint situated in the vicinity of B. This is in accordance with fig. 3.

In fig. 4—6 we will assume $\frac{y_1}{y} > \frac{x_1}{x}$ in order to remain in accordance with the direction of the boilingpointcurves, situated in the vicinity of B. As $\triangle W_y$ and $\triangle W_x$ are both negative, it follows from (14) and (15) that $dT_y < 0$ and $dT_x > 0$. On a boilingpointcurve situated in the vicinity of B the pressure, therefore, increases from the terminatingpoint on BA ($dT_x > 0$) and it decreases from the terminatingpoint on BC ($dT_y < 0$). In conjunction with the length of the parts, cut off by the curves from the sides BA and BC, we may express this also in the following way: along a boilingpointcurve situated in the vicinity of B the temperature increases in that direction, in which this curve comes nearer to B (fig. 4—6).

In the case sub *a* $\triangle W_x$ and $\triangle W_y$ are both positive, we now find the same rule as above for the change of temperature along a boilingpointcurve situated in the vicinity of B.

We may give a short résumé of some of the previous results in the following way. For this we assume that in the equilibrium solid B + liquid B + vapour B the limit-ratio of C is greater than that of A.

a) The two binary P,T-curves proceed from the point B towards lower pressures; consequently no point of maximumpressure occurs [$\triangle W_x > 0$ and $\triangle W_y > 0$; case sub *a*]. A boilingpointcurve situated in the vicinity of B cuts off from the side BC a greater part than from the side BA. The curve comes on decrease of P within the triangle.

b) One of the two binary P, T-curves proceeds from B towards lower pressures and one towards higher pressures, consequently one point of maximumpressure occurs [$\triangle W_x > 0$ and $\triangle W_y < 0$; case sub *b*. fig. 3]. The boilingpointcurve cuts off under pressures, somewhat higher than P_B, a part from BC, under pressures, somewhat lower than P_B, a part from BA. The curve remains, therefore, within the triangle as well on increase as on decrease of P.

c) Both the binary P, T-curves proceed from the point B towards higher pressures; consequently two points of maximumpressure occur [$W_x < 0$, $\triangle W_y < 0$; case sub c; fig. 4—6]. A boilingpointcurve situated in the vicinity of B cuts off from the side BC a smaller part than from the side BA. The curve comes, on increase of P, within the triangle.

In each of the cases, mentioned sub a, b, c, the temperature along a boilingpointcurve situated in the vicinity of B, increases in that direction in which this curve comes nearer to B (figs. 3—6).

(*To be continued*).

Chemistry. — "*Studies in the Field of Silicate-Chemistry: I. On Compounds of Lithiumoxide and Silica.* By Prof. Dr. F. M. JAEGER and Dr. H. S. VAN KLOOSTER. (Communicated by Prof. P. VAN ROMBURGH.)

§ 1. In connection with a series of investigations going on in this laboratory, on natural and synthetical lithiumaluminiumsilicates, it seemed to us of importance once more to take up the study of the binary system: lithiumoxide-silica, by means of the equipment and methods, which are now at our disposal; only in this way it seemed to us possible, to obtain thermical data, which are reliable and reducible to the nitrogen gasthermometer. At the same time we hoped to get information on the origin of in some respects rather strongly deviating results of earlier investigators, who have occupied themselves also with the study of these lithiumsilicates.

The two-componentsystem: Li_2O—SiO_2 has already several times been an object of research; thus some time ago by one of us[1]), using the method, already so often successfully employed upon metal-alloys, of the crystallizationphenomena on cooling, which will show themselves in such binary mixtures of varying composition. Later it was studied in the same way by ENDELL and RIEKE[2]), who of course in general also came to the same results, but who were not able finally to answer the question, if a third compound, the lithiumbisilicate, could separate from molten mixtures, like the ortho-, or meta-silicate.

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[1]) H. S. VAN KLOOSTER, Dissertatie Groningen (1910); Zeits. f. anorg. Chemie **69**, 136 (1910).

[2]) K. ENDELL und R. RIEKE, Sprechsaal, **44**. No 46 (1910); **45**. No 6 (1911).

Again another problem originated from a publication of G. **Friedel**[1]), who gave the description of a second modification of the metasilicate; this new modification was never obtained either by **Wallace**[2]), or by **Endell** and **Rieke**, or by ourselves from a molten mass. On the occasion of a renewed meltingpointdetermination, made by the first of us[3]) in 1910 at the Geophysical Laboratory in *Washington*, a new indication of an eventually appearing inversion was not found; at the same time it was once more demonstrated by this study, that even in this relatively favorable case, where the liquid was highly movable and the crystallization-velocity of the silicate could be considered as exceptionally great, the "coolingmethod" was by no means adopted, to give reliable and reproducible results. Other factors in the earlier determinations, e.g. the use of crucibles and tubes of porous carbon, and the insufficient control of the variations in chemical composition of the studied mixtures, caused by the volatility of the lithium-oxide, and finally the impossibility to reduce the existing thermical data to the scale of the nitrogengasthermometer, — seemed to us a series of reasons, to take up a new study of this binary system by means of the gradually developed exact methods[4]).

§ **2.** The necessary binary mixtures were prepared from the purest lithiumcarbonate and from pure, ground quartz of American origin. The lithiumcarbonate was dried at 100° C.; there was a loss of weight of only 0,05°/$_0$. Only sodium could be detected spectroscopically; the quantity was however so small, that it could not be determined by weight, using the amylalcohol-method. A trace of iron was found also, but scarcely sufficient to give a reaction with potassiumsulfocyanide as a pale pink colouring of the solution. The lithium was weighed as lithiumsulphate; determined: 18,72°/$_0$ *Li*, calculated: 18,79°/$_0$ *Li*.

The quartz lost on heating on the blast no more than 0,01°/$_0$; a small trace of iron, less than 0,03°/$_0$, appeared to be the single impurity. On evaporating with hydrofluoric acid in a platinum-dish, no residue was left; the used quartz therefore can be considered as pure SiO_2.[5])

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[1]) G. **Friedel**, Bull. de la Soc. Minér. **24**, 141 (1901); **Hautefeuille** et **Margottet**, Compt. Rend. **93**, 686 (1881).

[2]) R. C. **Wallace**, Zeits. f. anorg. Chemie, **63**, 1 (1909).

[3]) F. M. **Jaeger**, Journ. of the Wash. Acad. of Sciences, **1**, 49 (1911).

[4]) F. M. **Jaeger**, Eine Anleitung zur Ausführung exakter physiko-chemischer Messungen bei höheren Temperaturen. Groningen, 1913.

[5]) Those preparations were supplied by **Baker** and **Adamson**; the used material is the same as at the Geophysical Laboratory in *Washington*, and employed for standardizing purposes.

According to this high degree of purity of the components, all the binary mixtures, employed in this research, were absolutely white. They were obtained by heating weighed quantities of both oxides in a finely divided state in platinum or nickel crucibles; this manipulation was done in small resistance-furnaces, at temperatures ranging from 900° to 1000° C., and every contact with a reducing atmosphere was carefully avoided. After grinding down the masses and sifting, they were treated in just the same way, etc., till the whole preparation was shown to have a homogeneous composition. Mixtures between ortho-, and meta-silicate were prepared from both these compounds in quite the same way. The preparations were analysed after HILLEBRAND's indications [1]), and always in duplo.

Every admixture of formed nickel-oxide was carefully avoided; mixtures rich in lithiumoxide however, needed to be heated in platinum crucibles, because they would dissolve otherwise finely divided nickel, which coloured the preparation with a beautiful violet hue. For instance the orthosilicate could be obtained in this way, as a splendid, intensively coloured, violet product. The study of mixtures, richer in lithiumoxide, corresponding with the composition of the orthosilicate was not possible in the usual way, both because of the volatility of the oxide at the prevailing temperatures, and by the fact, that the lithiumperoxide Li_2O_2, generated at higher temperatures, will very quickly attack the platinum and the wires of the thermoelements; the platinum is superficially coated with a dull olive-green or greenish-yellow layer, and every accurate temperature-measurement thus gets practically impossible. Experiments, made in hermetically closed platinum-vessels however, have given many good results, as will be described further on, in § **12** of this paper.

§ **3.** The temperatures of equilibrium were determined in the way always used in this laboratory. A WOLFF-potentiometer (resistance: 83 Ohm) with three decades, and with a constant resistance of the galvanometer-circuit (WHITE—DIESSELHORST), was employed, in connection with a sensitive AYRTON-MATHER-movingcoilgalvanometer, with high resistance, and short period, to compensate the momentaneous electromotive force of the thermoelement; the galvanometer was calibrated and adjusted in such a way, that one microvolt corresponded with a millimeter on the scale. The observations, made with our thermoelements I and II (platinum and platinumrhodium (10°/₀)-alloy) could be compared immediately with the nitrogengas-thermometer, by means of calibration with a standardelement, cali-

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[1]) W. F. HILLEBRAND. Analysis of Silicate and Carbonate Rocks, 2nd. Edit. 1910.

brated in *Washington*, and by determination of the meltingpoints of Na_2SO_4 (884° C.), Li_2SiO_3 (1201° C.), synthetical diopside (1391° C.), and synthetical anorthite (1552° C.), with each of the three mentioned thermoelements successively. The potentiometer-current was kept constant at 0,002 Ampères; two **Weston**-cells, connected in series, and a **Wolff** auxiliary-rheostate, served as standard-electromotive force; the **Weston**-cells were constructed and controlled several times at the Physical Laboratory of the University. The furnaces used were platinum-resistance-furnaces with the heating-coil inside; they had the usual type, and their regulation was executed by means of a decade-rheostate of manganin-wire. The heating-current was direct current of 110 Volts and 20 or 30 Ampères.

§ 4. *The components.*

With respect to the components themselves, the following data may be given. The relation between the three modifications of the silicumdioxide: SiO_2, can be esteemed established in general lines after the recent, most accurate research of C. N. **Fenner** (Amer. Journal of Science, **36.** 331 (1913)).

The inversiontemperature for β-quartz $\rightleftarrows$ tridymite lies at 870° ± 10° C.; in the same way that for tridymite $\rightleftarrows$ cristobalite is determined at 1470° ± 10° C. The three modifications are enantiotropic forms, but the transformation-velocity is very small, and retardation-phenomena, even in an enormously high degree, are almost always present. This is the reason, why in nature some modifications of SiO_2 often occur within the stability-field of other forms.

Then there is at 575° C. an inversiontemperature for α- → β-quartz; at 117° C. one for α- → β-tridymite, at 163° C. one for β- → γ-tridymite; these inversions occur relatively fast. Probably the α-, and β-forms of cristobalite are in less or more stable equilibrium with each other at temperatures, situated between 198° and 274° C. The relations of those modifications to each other are very complicated, but of no direct interest for the present study.

The meltingpoint of cristobalite is very close to 1625° C.; the liquid is a very viscous mass, which by rapid cooling changes into the wellknown "glass".

Quartz is optically easy to discriminate from both the other forms, by the great differences of the refractive indices; the discrimination between tridymite and cristobalite however is rather difficult.

The refractive indices of quartz are: $n_e = 1.553$ and $n_o = 1.544$; those for tridymite are: $n_\alpha = 1.469$, $n_\gamma = 1.473$, while the true angle of the optical axes $2V =$ about $35^1/_2$°. For cristobalite these values are: $n_\alpha = 1{,}484$, and $n_\gamma = 1{,}487$.

The *lithiumoxide: Li_2O* is only sparely known up to this date. A description of it is to be found in an instructive paper of L. Troost [1]), whose data we in general could confirm. He obtained the oxide from lithiumcarbonate, by heating it at a high temperature in the presence of coal in a platinum-crucible, and also by heating the nitrate of lithium in silver crucibles at a red heat. The burning of lithium in oxygen gave only partial results, as the protoxide: Li_2O_2 was formed. The presence of this peroxide causes the yellow colour of the product. Troost describes the Li_2O as a white compound, with cristalline rupture. We prepared the pure oxide after the method of De Forcrand [2]), by heating lithiumcarbonate in a platinum vessel at 830°—900° C., while a current of dry hydrogen is run over it continuously. We obtained in this way an absolutely white, cristalline product, which makes the impression of having been melted. This however is not the case, as the aspect is caused by the melting of the carbonate itself before its decomposition. For, as we found, the oxide does *not* melt under these circumstances, but can sublime already under 1000° C.

We were able to confirm Troost's observation, that *pure Li_2O* does *not* attack the platinum, even at very high temperatures, but that the metal is attacked however, as soon as the oxide is heated with it in an oxidizing atmosphere. The cause of this phenomenon is the resulting peroxide, which attacks the platinum most intensily, and gave to it the yellow or olive-green colour, which we have also observed, whenever the lithiumorthosilicate was heated with the metal. The view of the French author, that in absence of oxygen, the Li_2O can be heated to a very high temperature, *without melting*, is also quite right. We have made some experiments, to determine its meltingpoint by means of the use of the "hollow thermoelement", — a method to be described further on, in the study of the orthosilicate and the mixtures, rich in Li_2O. It was found then, that a heating to 1570° C. (about 16400 M.V.) caused only a baking together of the powder to a very hard mass, which was coloured slightly yellowish by a trace of Li_2O_2, formed from Li_2O and the small quantity of air, present in the platinum-bulb; however even now the mass was probably not yet molten, nor at 1625° C., as we found afterwards. Because the platinum is very soft at these tempe-

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[1]) L. Troost. Ann. de Chim. et de Phys. (3). **51**. 144, (1857).

[2]) De Forcrand. Compt. rend. **144**. 1402, (1907).

ratures, the platinumbulb was inflated to a balloon, however without bursting.

Further we were able to determine the refractive indices and the specific gravity of the pure oxide. Under the microscope the compound appears as cristalline, irregularly shaped scales, with very weak birefringence. Often they seem to be wholly isotropous, as if they were glass. It may be, that the substance is finally yet of regular symmetry, for the weak birefringence often makes the impression of being only localised by tensions in the mass, more than of a real crystallographical anisotropy; and we found neither in any case an interference-image in convergent polarised light, able to prove that the compound belongs to one of the uniaxial classes. Once some trigonally shaped plates were observed, which looked like flat tetrahedrons or trigondodecahedrons; but it was impossible to prove this view more exactly. The refractive index was found by immersion: $n_D = 1{,}644 \pm 0{,}002$; so the refraction is relatively high, this giving some evidence of the fact, why a great many lithiumaluminosilicates, which are rich in Li_2O, show higher refractive indices, if they are richer in the oxide.

The specific gravity was determined by means of a pycnometer, with ortho-chlorotoluene as a liquid; before it was found, that the oxide does not attack this liquid in any appreciable way. As the most probable value (from three determinations), we found: $d_{4^\circ} = 2{,}013 \pm 0{,}015$, at 25°,1 C.

The oxide dissolves slowly into water, without giving a great heat-effect. The solution shows very strong alkaline reaction; it tastes lixivial and at the same time somewhat bitter. With acids no development of CO_2 was observed; so the product may be declared free from carbonate.

§ 5. We have now given in the following table the obtained results with mixtures of different composition; the numbers in the 7th, 8th, 9th and 10th columns are reduced on the gasthermometerscale of Day and Sosman [1]), this being at the moment the most accurate one. The composition of each mixture was determined *after* each experiment by direct analysis, according to Hillebrand's [2]) indications for the determination of the silicic acid. The thermoelements used, were I in the furnace, II in the mass; they were read alternately every half minute. Even with masses of hardly 1,5 gram, the heat-

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[1]) A. L. Day and R. B. Sosman, Carnegie-Publication No. 157 (1912).

[2]) W. F. Hillebrand, loco citato.

effects could be fixed on the temperature-time-curves very accurately; and if the furnace was run at a higher speed, again these temperatures were reproducible within ca. 1° C; they therefore can be considered as temperatures of true equilibrium.

Meltingpointdiagram of the Binary System: Li_2O—SiO_2.
(Thermoelement II placed in the mass).

Number of Experiment:	SiO_2 in Proc. of Weight:	SiO_2 in Proc. of mol.	Observed Temperatures in Int. Microvolts:		Observed Temperatures in ° C.		Corr. Temp. in intern. Microvolts		Corr. Temp. in ° C.	
			1st Effect	2d Effect	1st Effect	2d Effect	1st Effect	2d Effect	1st Effect	2d Effect
0	91.8	84.7	9902	—	1029	—	9866	—	1025.5	—
1	89.0	80.0	9919	—	1030	—	9883	—	1027	—
3	85.3	74.2	9922	—	1030.5	—	9886	—	1027	—
4	82.1	69.4	9920	—	1030.5	—	9884	—	1027	—
5	79.6	65.9	9972	—	1035	—	9936	—	1032	—
6	75.7	60.7	9982	10958	1036	1118	9946	10918	1032.5	1115
7	71.1	54.9	9912	11624	1029.5	1174.5	9876	11580	1026	1170.5
8	66.67	49.7	—	11992	—	1205	—	11944	—	1201
9	63.9	46.7	9800	11908	1020	1198	9764	11860	1017	1194
10	62.4	45.1	9854	11622	1025	1174	9818	11578	1021.5	1170.5
11	57.4	40.0	9872	10680	1026.5	1094	9836	10640	1023	1092
12	52.8	35.6	9870	10732	1026.5	1096.5	9834	10692	1023	1097
13	50.7	33.7	9850	11600	1024.5	1172	9814	11556	1021	1169.5
*14	49.9	33.0	9736	12154	1014.5	1218	9700	12106	1011	1215
15	49.8	32.9	9812	12448	1021	1243	9776	12402	1018	1239
*16	49.2	32.4	—	12634	—	1258.5	—	12590	—	1255
17	49.7	32.8	9826	12440	1022	1238	9790	12394	1019	1238.5

* The marked preparations must accidentally have been changed before analysis; we had however afterwards no means to ascertain this.

It may be remarked, that a preparation, having exactly the composition of the orthosilicate, always gave a slight heat-effect, corresponding with a eutectic temperature. We were able to show, that the cause of this phenomenon is the high volatility of the Li_2O: after one single meltingpointdetermination, already a loss of Li_2O

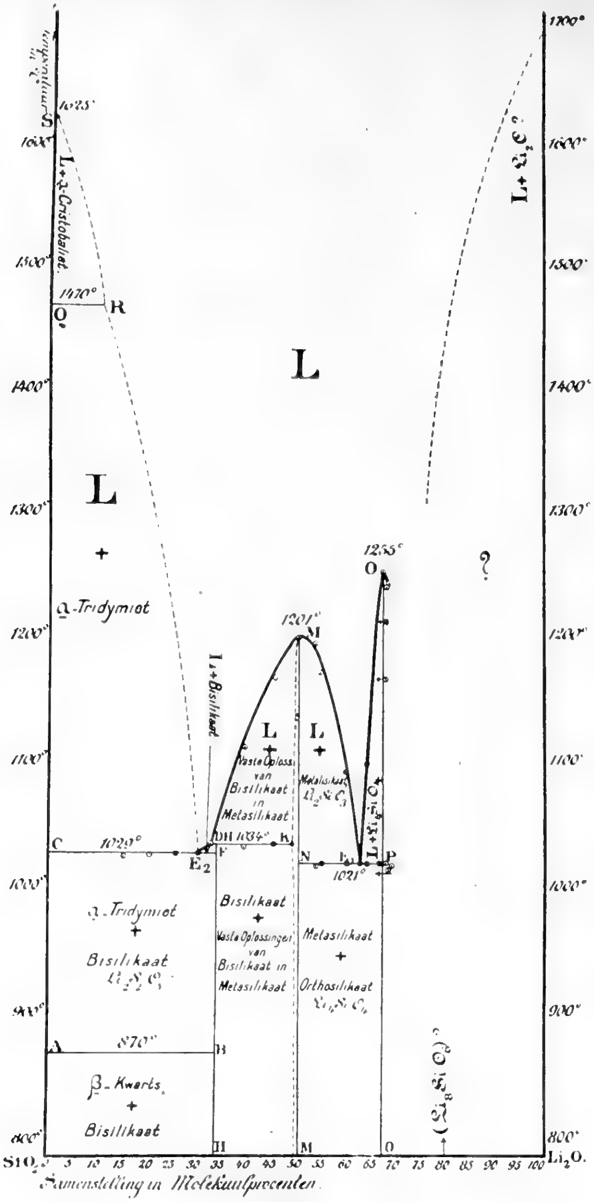

Fig. 1.

Temperatuur = Temperature. Cristobaliet = Cristobalite. Tridymiet = Tridymite. Bisilikaat = Bisilicate. Vaste oplossing van Bisilikaat in Metasilikaat = Solid solutions of Bisilicate in Metasilicate. β-Kwarts = β-Quartz. Samenstelling in Molekuul-procenten = Composition in Molecule-procents. Orthosilikaat = Orthosilicate.

of 0.4% could be stated. We finally obtained a temperature-time-curve, in which the eutectic effect had disappeared, starting with a mixture, which showed a small excess of the lithiumoxide; the meltingpoint was now at 12598 M.V. (corr.) corresponding with 1255°,5 C. This temperature we must consider as being the true meltingpoint of the orthosilicate, with an uncertainty of about

± 3° C, caused by the variability in chemical composition as a result of the extraordinary volatility of the lithiumoxide, which will sublime already at temperatures, much lower than this meltingtemperature. Further below we will give the determinations of the meltingpoint of the orthosilicate by means of a closed crucible and a new method of observation; we shall see, that the true meltingpoint does not differ appreciably from the here given value.

In fig. 1, we have composed these numbers graphically in the usual way. At the same time also the results, of our experiments, concerning the determination of the field, in which the bisilicate can exist in contact with the liquid, are indicated in this figure. The last mentioned determinations have given us much trouble, because great difficulties were connected with the limitation of this very narrow field of stability of the compound. We have only succeeded by numerous quenching-experiments: preparations, heated during a long time on known and constant temperatures, were momentaneously chilled, and investigated in all details by means of the microscope. Only in this way the place of the bisilicate in the series could be fixed with sufficient accuracy; the experiments on this subject are described afterwards.

As a general result, we can thus say, that there are *three* compounds: $Li_2 Si O_3$, $Li_4 Si O_4$ and $Li_2 Si_2 O_5$; the compound $Li_8 Si O_6$, proposed by Niggli on a very weak argumentation in no case exists in contact with a molten mass; while the compound $Li_2 Si_2 O_5$ has evidently no real meltingpoint, but only a transformationtemperature at 1032° C., at which it decomposes with deposition of some metasilicate, or of a solid solution of a little of the bisilicate in an excess of metasilicate [1]). We think we are right in this last view, because the refractive indices of the needles of $Li_2 Si O_3$, which are deposited at this temperature, have evidently somewhat lower values (1.57 instead of 1.585 etc.), than the pure metasilicate.

The composition of both the eutectic mixtures E_1 and E_2, can be indicated by:

E_1 .... (1022° C.): 55 Proc. of Weight SiO_2 = 37.7 Mol. Proc. of $Si O_2$.

E_2 .... (1027° C.): 82,1 Proc. of Weight SiO_2 = 69.4 Mol. Proc. of $Si O_2$.

§ 6. The *lithiummetasilicate* crystallizes from the thin molten mass very rapidly; for this reason we succeeded in obtaining a "glass"

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[1]) P. Niggli, Journ. of Amer. Chem. Soc. (1913); Zeits. f. anorg. Chem. 84, 263. (1913). In fig. 1 is wrongly written 1034° C, instead of 1032° C

of this substance only by cooling very small quantities of the compound. The cristallized liquid consists of long, opaque, porcelain-like looking needles, which show a principal and very complete cleavage in the direction of their elongation; heavier individuals therefore will decay very easily in a number of thin, felty needles, showing normally orientated extinction. In the zone of the longer axis we could measure some angles between 59° and 61°; this form of the silicate seems to be the same as that, described by Hautefeuille and Margottet as rhombic, with pseudo-hexagonal symmetry. Doubtless the silicate is biaxial, and probably monoclinic; the plane of the optical axes parallel to the elongation of the needles, and perhaps almost perpendicular to the formes }100{ or }001{.

Fig. 2.

Lithiummetasilicate (Enlargement 50 ×) (immersed in a liquid).

The silicate used was the same, as formerly described by one of us [1]). Its analysis gave the following values:

Sio_2	$66.60^0/_0$
Li_2O	$32.80^0/_0$
Na_2O	$0.51^0/_0$
Fe_2O_3	$0.02^0/_0$
CaO	$0.03^0/_0$
	$99.96^0/_0$

There is thus about $0.3^0/_0$ Li_2O too little. The metasilicate is decomposed by water, however much more slowly than the ortho-silicate. Finally however the water shows some alkaline reaction. The meltingpoint was determined with Sosman's element C at 11954 M.V., corresponding with 1201°.8 C.; Day and Sosman determined 1200°.6 C. Another preparation, (Crenshaw), whose analysis gave the following numbers:

SiO_2	$65.89^0/_0$
LiO_2	$32.83^0/_0$
FeO	$0.05^0/_0$
H_2O	$1.2\ ^0/_0$
	$99.97^0/_0$

had a meltingpoint of 11930 M. V., or 1199,°8 C.; with the thermoelements G and H of Sosman and Day. The meltingpoint of pure

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[1]) F. M. Jaeger, Journ. of Wash. Acad. of Sciences **1**. 49. (1911).

Li_2SiO_3, can be indicated thus at 11944 ± 12 M. V. or 1201° C. ± 1°. The meltingpoint can be localised so sharply on the heating-curves, that the compound can be used with success for calibration purposes; the temperature of equilibrium is here really *in*dependent of the speed of heating, in very wide limits.

By means of the method of immersion, the refractive indices for sodiumlight were determined on:

$n_D = 1{,}609 \pm 0{,}004$, for vibrations parallel to the direction of elongation of the needles,

$n_D = 1{,}584 \pm 0{,}002$, for vibrations, orientated perpendicularly to the first direction.

The birefringence is strong and of positive character, being about 0,025. The specific gravity at 25° C. was: $d_4 = 2{,}520$. In fig. 2 a microphotograph of the crystallized meta-silicate between crossed nicols is given while this is immersed in a liquid of about the same refractive index.

With the aid of the method of quenching, used in this laboratory with substances, heated at a constant temperature during a long time, we were able to get some *glass* of the metasilicate. As the compound crystallizes extraordinarily rapidly, it was only possible to succeed by using very small quantities of the silicate, about 0,05 to 0,1 gram, wrapped in platinum-folium, and suddenly chilling them by means of cold mercury. The refractive index of this glass was found to be: $n_D = 1{,}548 \pm 0{,}002$ at 25° C; thus it appears to be appreciably less than the smallest index of the crystallised substance. The specific gravity of the glass was determined at: $d_4 = 2{,}330$, thus being at 25° C. also much lower than for the crystallized substance.

§ 7. We found no indication whatever of an inversion temperature in heating and cooling our preparation; also in the microscopical work we were not able to find any other modification of the metasilicate than the one just described.

However G. FRIEDEL [1]) described in 1901 another form of lithiummetasilicate, which he claimed to be trigonal and, strangely enough, to be homeomorphous with phenakite. He obtained this form of Li_2SiO_3 by heating the product, obtained by the reaction between Li_2O, SiO_2, and muscovite in solution at 540° C. under pressure. His results do not agree with those of MARGOTTET and HAUTEFEUILLE [2]), who used $LiSi$ as a flux, and obtained needles, to which they attribute rhombic symmetry, with pseudo-hexagonal character.

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[1]) G. FRIEDEL, Bull. de la Soc. Miner. de France, **24**, 147 (1901).

[2]) HAUTEFEUILLE and MARGOTTET, ibid. **4**, 241 (1881); Compt. rend., loco cit.

Just because neither we, nor our predecessors, ever found any indication of another form of the metasilicate, than the mentioned biaxial one, we wrote to Mr. FRIEDEL, asking him to send us a sample of his modification. We wish to offer this mineralogist our best thanks once more, for his aid and the trouble he has given himself, to help to elucidate the complicated problem of those form-deviations.

The preparation sent to us, soon appeared to be an aggregation of flat needles, often radially ordered, *which were however doubtless biaxial.* As was indicated on the label, they were obtained from molten $LiCl$, showed a pale pink tinge, and an extinction, directed perpendicularly and parallel to their elongation; the refractive index for vibrations parallel to their direction of elongation, was: $n_D = 1{,}585 \pm 0{,}003$, (being thus identical with that of our needles, perpendicularly to their elongation), while the refractive index for vibrations orientated perpendicularly to the above, was: $n_D = 1{,}563 \pm 0{,}002$, from which there results a birefringence of about: 0,022, being thus only slightly less than for pure metasilicate. The flat needles showed at their top-, and base-end, two small faces, making with the longer edge of the crystals angles of respectively: 114°, 126°, and 120°.

In an experiment, where finely crushed Li_2SiO_3 was heated during eight hours with molten $LiCl$ at 900° C. no other crystals were obtained than the ordinary, biaxial needle-shaped form, which we described already.

For another preparation of Mr. FRIEDEL, (with the number IV), also obtained from molten $LiCl$, which preparation contained some metallic copper [1]), and some $LiCl$, we found: $n_D = 1.584 \pm 0.002$, and $n_D = 1.574 \pm 0.002$, the directions of the vibrations corresponding with those, given earlier. The birefringence is thus now: 0.010 or 0.012; evidently the refractive index for vibrations in the elongation-direction of the needles, seems to be *variable.* We think it not improbable, that a slight admixture in solid solution, of the bisilicate: $Li_2Si_2O_5$ with its lower refractive index: ca 1.54, must be supposed, to be the cause of this variability.

§ 8. After having received the account of these experiments, Mr. FRIEDEL was so kind as to repeat his experiments of 1901. Further he succeeded in finding again a preparation of the year 1898 (C; exp. I, 1898), prepared by heating a solution of 2,5 grams of dried SiO_2 and 0.65 gram of Li_2O, with 6 grams of muscovite at 540° C.

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[1]) From the lining of the steelbomb, used in this and other experiments.

during 27 hours in a steelbomb lined with platinum. Of this preparation, looking also like radial bundles of needles with trigonal symmetry, we obtained some sections, normal to the axis of the needles. In convergent polarized light it was in reality possible to observe an interference-image, closely similar to that of an optically uniaxial crystal of positive character; however, on moving the section and rotating the table of the microscope, the image did not remain unaltered, but the black cross opened its branches somewhat, and it was immediately evident, that a *biaxial* crystal, however with a very small axial angle, was present. Of yet higher importance however seemed the fact, that the crystalplate showed itself in parallel polarized light, *to be composed of a number of sectors* (fig. 3); in every sector the black cross between crossed nicols seems to open itself somewhat. It is hardly to be doubted, that a pseudo-symmetric aggregation is present here, with noticeable optical anomalies.

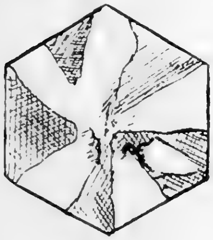
Fig. 3.

The repeated experiments of Mr. Friedel gave, as he wrote us, no other crystals whatever, than *biaxial* ones, with very small axial angles, amounting occasionally to about 27°. The experiments were made in these cases, by heating 2,68 grams of dry SiO_2 and 0.885 grams of Li_2O (as hydroxyde) in solution, with a known quantity of finely divided muscovite, at 545° or 550° C. during 30 hours. Also without addition of mica, and at lower as well as at higher temperatures, the same results were obtained. (*A* and *B*, experiment XI, 1913). Although all conditions of the earlier experiment I, 1898) were as much as possible fulfilled, the obtained needles appeared however, *always to be biaxial:* a form of *complete* trigonal symmetry was never produced in any of these cases.

The birefringence of the pseudo-trigonal needles of preparation (I, 1898) was about: 0.021; that of the crystals from molten $LiCl$ was: 0,023 values do not differ noticeably from that, obtained by us formerly with the biaxial silicate.

The preparations *A* and *B*, and XI, 1913, were investigated in convergent and in parallel polarized light. Some sections, perpendicular to the axis of the needles, are reproduced in fig. 4. Doubtless it must result from this, that very complicated individuals and polysynthetic twins of lamellae, crossing under 60°, are present; the pseudo-trigonal habitus is caused thus by polysynthetic twinning.

The composing lamellae are all biaxial, the axial angle is very small, and rarely exceeds, as said already, 27°. By means of the immersion-method we were able to determine with some of these needles the following values for the refractive indices: $n_D = 1.600 \pm 0.003$ for vibrations parallel to the longer axis of the needles, and: $n_D = 1.584 \pm 0.002$ for vibrations, perpendicular to the first named.

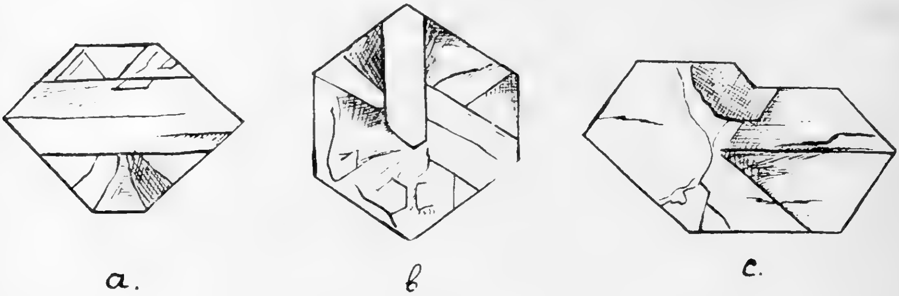

Fig. 4.

The question, whether the composing lamellae must be considered, in agreement with Hautefeuille and Margottet, as rhombic, is in our mind, very doubtful. As already the French author himself suggested, it is more probable to suppose *monoclinic* symmetry, and a pseudo-trigonal aggregation of these monoclinic individuals. Indeed, by such a polysynthethic twinformation, no pseudo-*trigonal*, but a pseudo-*hexagonal* aggregation woult result, because the original axes of binary period would involve a symmetry-axis of the whole structure, having a period of 60°.

The specific gravity of the modification (I, 1898) being: $(d_{15^\circ} = 2,529$, is in complete agreement with that of our biaxial metasilicate, which had: $(d_{4^\circ}^{25^\circ} = 2.520$ at 25° C.

Summarizing all these data, we must conclude from our experience in this matter, that the so-called pseudo-trigonal modification of the metasilicate can be *no new* modification of Li_2SiO_3, but only a polysynthetic twinformation of the original biaxial form, imitating very closely a true trigonal individual.

This form with its apparent symmetry, must in questions of thermodynamical equilibria be considered as *the same phase* of the compound, which is deposited from the molten mass ordinarily as long, truly biaxial needles. In accordance with experience, brought up to this date by the study of such mimetic crystals, it is just quite clear, that no appreciable thermic effect, indicating some noticeable, sudden difference in the total energy of the system, could be detected in our experiments.

§ 9. *The lithiumbisilicate*: $Li_2Si_2O_5$ crystallizes from molten binary mixtures of the same chemical composition, in the form of the great, flat crystals, which are characterised by their tabular shape and their peculiar aspect. Often they are recognisable (Fig. 5) by a system of cleavage-directions, crossing each other almost normally in three directions of space; the plates, as if covered with a fine network, are thus often bordered by right angles. The symmetry seems to be rhombic, or probably monoclinic; the crystals are biaxial, with positive character of their birefringence, which is about 0,020, — being slightly less than for the metasilicate. The apparent axial angle is probably rather great; more or less complicated twins are present. The figures 6 and 7 may give some representation of the habitus of this compound, as it looks between crossed nicols. The refractive indices are about: 1.545 and 1.525; it is very difficult to determine them accurately, because the crystals are intergrown with fine, felty needles of tridymite, or in some preparation with those of the metasilicate. The peculiar cleavage-directions are in every case most typical for this compound.

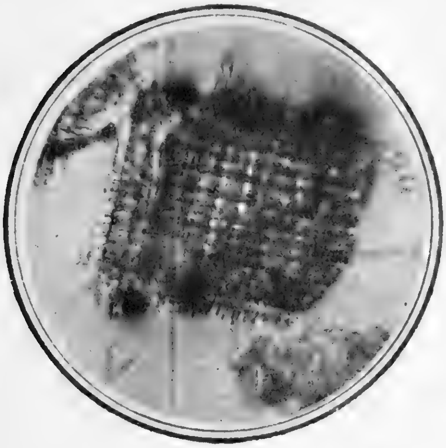

Fig. 5. Lithiumbisilicate; cleavage-directions (enlargement 500 ×).

The specific gravity of the bisilicate was pycnometrically determined on: $d_{4^\circ}=2,454$ at 25°.1 C.

It was a difficult thing to fix the borders of the stability-field of this compound, in contact with a binary liquid. We succeeded, by heating preparations of different composition, inclosed in thin platinum-folium, at a constant temperature during a time ranging from 20 to 60 minutes, in a quenching-furnace, and chilling the preparations then suddenly in cold mercury; in this way the momentary state of the mixture is fixed, and can be studied by accurate microscopical investigation.

The results of those experiments were the following:

Preparation N°. 3. Analysis: Weight Proc. of SiO_2 (= 74.2 Mol. Proc.).

Temperature in M.V.:

8890 Wholly crystalline; much bisilicate, very little tridymite.

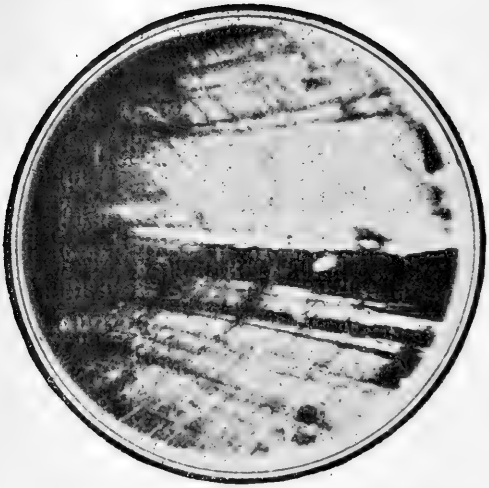

Fig. 6. Lithiumbisilicate. (cleavage-directions; enlargement: 50 times).

Fig. 7. Lithiumbisilicate. (Enlarg. 50 times).

Temperature in M.V.	
9920	Little bisilicate; mostly feebly birefringent aggregates of tridymite.
9930	Idem.
10370	Much glass, in which imbedded extremely feebly birefringent needles.
10970	Idem.
11570	Idem.
11770	Idem.

Preparation N°. 4. Analysis: 82.1°/₀ SiO_2 (= 69.4 Mol. Proc.).

Temperature in M.V.:	
9910	Crystalline, principally bisilicate, no tridymite in any appreciable quantity.
9930	Very little bisilicate, many feebly birefringent aggregates; a little glass.
9970	All glass.

Preparation N°. 5. Analysis: 79.9 °/₀ SiO_2 (= 66.6 Mol. Proc.).

Temperature in M.V.	
9930	Bisilicate in typical form, often undulatory extinction, and finely intergrown with needles of impure metasilicate $n_D = 1.56$ or 1.57.).

Temperature in M.V.	
9950	Idem.
9962	About 10 °/₀ glass; further as mentioned above.
9985	About 50 °/₀ glass; imbedded bisilicate and needles.
9990	About 70—80°/₀ glass; needles of apparently impure metasilicate $n_D = 1.57$).
10005	About 90 °/₀ glass; needles with $n_D = 1.56$ or 1.57.
10040	Almost all glass ($n = 1.536$); locally a few needles.

Preparation N°. 6. Analysis: 75.7 °/₀ SiO_2 (= 60.7 Mol. Proc.).

Temperature in M.V.:	
9930	Felty aggregations of metasilicate, intergrown with much bisilicate.
9990	About 5 °/₀ glass; metasilicate with $n_D = 1.57$.
10030	About 80 °/₀ glass; felty birefringent needles.

We are of opinion, that in accordance with these results, the field, in which the bisilicate can exist in contact with a binary liquid, can be indicated as done in fig. 1; the compound must melt at 1032° C. under dissociation into metasilicate, and give a binary liquid of slightly varied composition. However, it seems, that no pure metasilicate is deposited, but a very dilute solid solution of the bisilicate in it; this we may conclude from the fact, that the refractive indices of the needles are always somewhat less than those of the pure compound.

§ 10. The third possible compound, existing in contact with its binary liquid, the *orthosilicate*: Li_4SiO_4, was prepared in quite the same way by heating of the finely divided, thoroughly mixed components. Although the mixture, in composition identical with the compound, could also in this case be melted with a blast, if in small quantity, it was necessary to keep the molten mass at 1500° C for some time, to be sure, that practically all carbondioxide is expelled. But then some Li_2O volatilizes, and thus the chemical composition must be corrected again and again, till the required composition is reached. If, as is the case in the *Fletcher*-furnace, there is some watervapour present, the mass obtains afterwards a very disagreeable odour of silicohydrogens. It seems, that the flame-gases generate platinum-silicides, which afterwards are decomposed by watervapour under generation of silico-hydrogencompounds. The platinumcrucibles are strongly attacked by the Li_2O_2, which forms from the orthosilicate, when melted in the air; the platinum is coloured greenish or yellow, while the mass itself often looks pale-pink.

The fact of the attacking of the platinum by the lithiumperoxide, made it impossible to obtain reliable measurements with mixtures, richer in Li_2O than the orthosilicate, because the thermoelements are spoiled in the same way as the crucibles, and are thus losing their calibration. This fact must be kept in mind also, when meltingpoint determinations of the orthosilicate are made.

The orthosilicate, if brought into cold water, is momentaneously hydrolised by it; the solution shows a strong alkaline reaction. Analogous decomposition finds place by the carbon dioxide and the humidity of the atmosphere.

The heating of the orthosilicate in nickel crucibles, as already mentioned, causes an intensive lilac colouring of the mass, probably by diffusion of metallic nickel from the walls into the central part of the substance. The colour is the same, as many nickel compounds with complex ions show; it is not improbable, that the nickel is present in these products in the colloidal form, as observed e.g. by LORENZ [1], in the electrolysis of some molten salts.

Microscopical investigation taught us, that the lilac product shows the same polygonal or almost round, very thin scales as the pure orthosilicate; however, they were now tinged homogeneously violet, and also often locally darker than in other places. These coloured crystals are noticeable *dichroitic*, as is often observed in crystals, which take some dyes in solid solution.

The refractive indices of this lilac substance did *not* differ appreciably from those of the pure compound. By means of the immersion-method, we found: $n = 1{,}595 \pm 0{,}005$ and $n_2 = 1{,}610 \pm 0{,}005$; the birefringence is fairly strong, and about: 0,015 to 0,020. Often a twinning is present, which reminds of that of albite. The specific gravity was determine dpycnometrically, in toluene, to be: $d_{4^\circ} = 2{,}392$ at 25,°1 C.; the coloured product showed a value slightly higher: $d_{4^\circ} = 2{,}415$ at 25°,1 C. Figure 8 may give a representation of the compound between crossed nicols; some twins are also shown in it.

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[1] Cf. among others LORENZ, Elektrolyse der geschm. Salze II. S. 40. (1905); Gedenkboek VAN BEMMELEN. (1910). p. 395.

Fig. 8. Lithiumorthosilicate. (Enlargem. 50 times; in immersion-liquid).

§ 11. The analysis of our product thus obtained, gave 50,8°/₀ SiO_2 and 49,2°/₀ Li_2O, while one calculates: 50,23°/₀ SiO_2 and 49,77°/₀ Li_2O. So there was an excess of 0,57°/₀ SiO_2, causing the small eutectic heat-effect at 1020° C. on the heating-curve. The meltingpoint of this substance, measured four times with the element S_4, was found successively (without correction) to be: 12463 M.V.; 12408 M.V.; 12399 M.V.; 12373 M.V.

The meltingpoint is thus continually lowered, which is caused by the fact, that more and more Li_2O evaporates. and some Li_2O_2 is generated at the same time. On cooling, retardation of the crystallization was observed to about 12280 M. V., depending upon the speed of cooling; then, a sudden rise of temperature, caused by the solidification of the mass was observed to 12320 M. V.

To find the true meltingpoint, we started therefore with mixtures, which had a slight excess of Li_2O; the experiment showed, that already after one single determination, a loss of 0,4 Li_2O could be proved, while a eutectic effect at 9775 M.V. became noticeable. Finally some heatingcurves were obtained, showing *no* eutectic effect; the crystallized product gave, on analysing, 50,0°/₀ LiO_2. With thermoelement II the meltingpoint was now 12590 M.V. (corr.), corresponding with 1255°,5 C. ± 3°.

By means of the method of the "hollow thermoelement" (vid. § **12**), we determined the meltingpoint to be: 1256° C.; as to the fact, that this temperature could eventually rather correspond to a three-phase-equilibrium, cf. § 12 and § 13 *i*.

The refractive indices of the scale-shaped crystals were measured by means of the immersion-method, and found to be $n_D = 1{,}614 \pm 0{,}003$ and $n_D = 1{,}594 \pm 0{,}003$. The birefringence therefore was fairly strong: about 0,020, perhaps somewhat less than for the metasilicate; the same albite-like twinning as with the lilac crystals was also observed in this colourless product.

The finely divided powder of the orthosilicate, like that of $LiOH$, stimulates intensively to sneezing.

§ 12. We have tried to gain some more data on the thermic behaviour of mixtures, whose composition was lying between that of Li_4SiO_4 and Li_2O, and more particularly, with the aid of a method, which possibly may open an important way in future, to get results in those cases, where one of the components is highly volatile, or changes in contact with the air. Therefore we shall describe it shortly. The method is this, that crucibles are made from the purest stock of platinum, like that used in drawing the wires of the thermoelements, which crucibles have the shape and size, reproduced in fig 9*a*. A platinumrhodiumwire of a thermoelement, about 0,6 m.m. thick, is soldered to it at the bottom by means of the oxygenflame; then the crucible is filled with the finely powdered material, with the aid of the small funnel and hollow stem; after cleaning it very well, a thick platinumwire of the same diameter as the stem is introduced into it, and the crucible is melted off then at the top. The platinumwire of the used thermoelement, also 0.6 m.m. thick, is soldered then with the oxygenflame at the top of the crucible, and the other wire is bent as shown in the fig. 9*b*. Both wires are isolated by means of porcelain capillary-tubes, and the whole apparatus then fixed in a Marquardt-tube and hung in the furnace. The crucible must be in the region of the furnace, where no appreciable temperature-gradient is present. In the immediate neighbourhood of the crucible a second thermoelement is fixed in position; then the meltingpoint of the substance can be determined in the usual manner, by reading both thermoelements alternately every half minute.

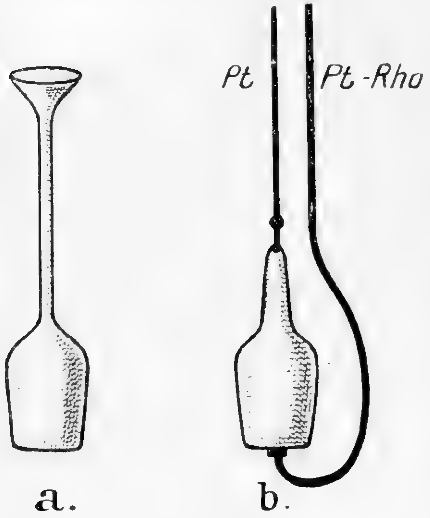

Fig. 9.

Some experiments with $Li_2\,Si\,O_3$ *immediately proved the method to be completely adapted for our purposes*: we found the meltingpoint not only as sharp as formerly, but also the undercooling- and solidification-phenomena gave perfectly analogous results, as in the case, where open crucibles were used. The meltingpoint of $Li_2\,Si\,O_3$, determined in this way, was found at an E.M.F. of 11968 M.V.; as the correction of the thermoelement however was determined to be —26 M.V., thus the temperature i.c. lies at 11942 M.V. or 1201° C.

We now tried first of all, to determine the meltingpoint of pure

Li_2O in this way, if free from peroxide. Although the temperature was increased up to 1625° C. this time, we were not able to find any heat-effect. The crucible was inflated like a balloon, but did *not* crack. After being opened, we found the powder baked together, however *not* molten. An unimportant trace of peroxide only was formed. Therefore we must conclude, that as Troost already pointed out, the melting-point lies very high, — higher than can be determined by means of our platinumresistance-furnaces and thermoelements. Probably the meltingpoint will be in the neighbourhood of 1700° C.

Thirdly we determined the meltingpoint of the Li_4SiO_4 quite in the same way, and found it (without any correction), in several determinations, at an E.M.F. of 12640 M.V., if the thick thermoelement (0,6 m.m.) was used. As the correction of it was —35 M.V. for this temperature, the true meltingpoint is **1256**° C. (G. Th.), thus not differing appreciably from the formerly obtained value. The heat-effect was not large; but if the thermoelement is fixed in a suitable way at the bottom, which must be bent a little inwardly, the heat-effect is clearly localised on the heating-curves. On cooling, we found a crystallization at 1249° C.

It is of course possible, that this temperature of 1256° C. indeed corresponds to a steep and not very extended maximum in the curve. However we made some more experiments, to find out the form of the curve for mixtures, which are still richer in Li_2O, by means of the described new method. With a mixture, corresponding to 54 weight-procents Li_2O (or 71 Mol. proc. Li_2O), we found a good observable heat-effect at 1405° C.; then the bulb cracked by the enormous vapour-tension. Thus it can be, judging from this, that the temperature of 1256° C. must be considered rather as a temperature of "transformation", at which the orthosilicate melts under dissociation into Li_2O, and into a liquid, whose composition is very close to that of the pure compound.

§ 13. *Microscopical investigations.* All preparations were microscopically investigated, and the results were in every case compared with those of the thermical determinations. It is an agreeable task to us, to express our thanks once more to Dr. F. E. Wright in *Washington* for his kindness and readiness to look over our preparations again, and for the information he has given us in some doubtful cases.

In general we can say, that the results of these investigations by means of the microscopical method agree fairly well in all respects, with the conclusions drawn from our thermical work. The preparations are ranged in the following, in series of increasing quantities of SiO_2.

a. 91.8 Weight Proc. SiO_2 (= 84.7 Mol. Proc.).

This preparation showed two components: firstly a substance of weak birefringence and a refractive index of about 1.480. It is present in irregular felty needles, spread through the other component, or in corns of indefinite boundaries. This substance seems to be no other than *α*-tridymite.

Another substance of stronger birefringence and of a positive character, with a refractive index of about 1.545 is seen accompanying it. The birefringence is about: 0.020, thus being a little less than for the metasilicate. This component is the bisilicate: $Li_2Si_2O_5$. Solid solutions between this compound and SiO_2, which we were inclined to suppose, seem after Dr. WRIGHT's judgment not to be present.

b. 89$^0/_0$ SiO_2 (= 80 Mol. Proc.). This preparation is in all respects analogous to the former one.

Fig. 10. 89 Weight Proc. SiO_2. (Enlargement: 50 ×).

Fig. 11. 85,2$^0/_0$ SiO_2. (Enlargement: 50 ×).

c. 85.3$^0/_0$ SiO_2 (= 74.2 Mol. Proc.).

The quantity of tridymite is considerably diminished; it is only present in exceedingly small needles. The bisilicate presents itself in tabular crystals, intergrown with tridymite. In convergent polarised light, the substance is shown to be biaxial; however the axial angle seems to be too large, to observe a complete interference-image. Sometimes the crystals have the aspect as if subjected to torsion.

d. 82.1$^0/_0$ SiO_2 (= 69.4 Mol. Proc.). This preparation is almost homogeneous, and consists of tabular crystals; the macroscopical aspect of the preparation gives already immediately the same impression. Most characteristic is the system of cleavage-directions which seem to cover the plates as with a fine net-work of lines in three directions, arranged perpendicularly to each other in space. The boundaries of the tables are often rectangular; they show normal extinction. The refractive indices are: 1.545 parallel to the axis of elongation of the crystals, and 1.525 perpendicularly to it. The birefringence is of positive character and about: 0.020.

Often twins or very complicated intergrowths occur.

e. 79.6°/₀ SiO_2 (= 66.0 Mol. Proc.).

The preparation is again fairly homogeneous. Only some fine needles are found locally on the table-shaped crystals, probably representing the metasilicate. This fact would prove, that the bisilicate will dissociate on melting. The birefringence is positive and about: 0.020; the refractive indices are found to be about: 1.545 and 1.530. Many parallel intergrowths, and polysynthetical twins seem to be present; the fine lines, indicating the system of cleavage-directions, are here most typical. Locally the preparation shows a little quantity of glass.

f. 75.7°/₀ SiO_2 (= 60.7 Mol. Proc.).

This preparation is inhomogeneous; longshaped needles, with $n = 1.585$ and normal extinction are intergrown with the grains and plates of the bisilicate. The refractive indices of the needles are somewhat less than those for pure Li_2SiO_3; we found e.g.: 1.595 and 1.569 in the same individuals.

g). 71.1°/₀ SiO_2 (= 54.9 Mol. Proc.).

The quantity of the metasilicate is considerably increased; for the remaining part just as *f*.

Fig. 12. 78,8 Weight Proc. SiO_2. (Enlarg. 50×).

h). 66.7°/₀ SiO_2 (= 49.7 Mol. Proc.).

Homogeneous. It is the Li_2SiO_3, with all properties, formerly indicated. The axial angle seems to be rather small.

i). 63.9°/₀ SiO_2 (=46.7 Mol. Proc.). In general lines this preparation resembles the former; locally small grains of the orthosilicate, with its weaker birefringence, but stronger refraction, are visible.

The following preparations are then analogous to *i*; the quantity of the metasilicate diminishes gradually, compared with the closely intermixed orthosilicate, which presents itself in round or polygonal corns, often twinned in a particular way. The preparations, which are in gross composition very close to Li_4SiO_4, show the crystals of the orthosilicate often in a highly altered condition; the immersion-liquids also seem to be attacked by the expelled alkali, and measurement is often impeded by it.

The fact, that the crystals of the orthosilicate appear often more or less attacked under the microscope, could make more probable the view, according to which the temperature of 1256° C. were rather a "transformation"-temperature than an ordinary meltingpoint; the compound would be converted thus into a liquid, with partial dissociation.

In the principal outlines we may say, that the binary diagram of SiO_2—Li_2O is known now. It will doubtlessly prove for the present impossible, to investigate the behaviour of the components at concentrations between orthosilicate and lithiumoxide in their complete details, because of the enormous volatility of this oxide at these extreme temperatures.

Laboratory of Inorganic and
Groningen, February 1914. *Physical Chemistry of the University.*

Physics. — *"The volume of molecules and the volume of the component atoms."* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of January 31, 1914).

I think I may assume as known that for normal substances the volume of the molecules expressed in parts of the gas volume at 0° and 1 atmosphere pressure may be calculated in a simple way by means of the critical quantities. When it is not yet taken into account that the quantity b of the equation of state decreases with v we find:

$$\frac{RT_k}{p_k} = 8\,b$$

$$\text{or}\quad \frac{T_k}{p_k} = \frac{8 \times 273}{(1+a)(1-b)}\,b,$$

in which b represents 4 times the volume of the molecules. If we do take into account that this factor 4 diminishes when the volume, as is the case for the critical state, has decreased to almost $2b$, we find by approximation:

$$\frac{T_k}{p_k} = \frac{7 \times 273}{(1+a)(1-b)}\,b_g$$

And if this factor 7 was really equally great for all substances, $\frac{T_k}{p_k}$ would be almost proportional to the size of the molecules. As it is not my purpose in this communication to calculate the exact numerical value of the size of the molecules, and in connection with this the perfectly exact numerical value of the component atom volumes, which perhaps is not yet feasible, among others on account of the imperfect knowledge of the accurate value of T_k and p_k, and as this communication more bears the character of a preliminary exploration of the territory, I shall assume the quantity $\frac{T_k}{p_k}$ as a numerical value, which is really, at least by approximation, proportional to the size of the molecules and by the aid of this value I will investigate what follows for the size of the component atoms from this size of the molecules. The quantities T_k and p_k are borrowed from the excellent Recueil des Constantes physiques by Messrs. ABRAHAM and SACERDOTE.

As I expected the simplest relations for the saturated hydrocarbons, I began with them, and the values of T_k, p_k, and $\frac{T_k}{p_k}$ follow here.

	T_k	p_k	$\frac{T_k}{p_k}$		calculated
Methane	191,2	54,9	3,483	CH_4	3,483
Ethane	305,16	48,86	6,2456	C_2H_6	6,243
Propane	370	45	8,2222	C_3H_8	9,003
Butane	not given.				11,763
Pentane	470,2	33,03	14,236	C_5H_{12}	14,523
Isopentane	460,8	32,93	14,	C_5H_{12}	14,523
Hexane	507,8	29,76	17,06	C_6H_{14}	17,283
Heptane	539,9	26,86	20,01	C_7H_{16}	20,043
Octane	569,2	24,64	23,1	C_8H_{18}	22,803
Decane	603,4	21,3	28,35	$C_{10}H_{22}$	28,323

For the increase of the molecular volume in consequence of the introduction of 1 atom C and 2 atoms H into the molecule CH_4, we successively find the values:

2,7626
2,37
2,668
2,7134
2,753
2,802
and with Decane—Ethane 2,781.

The inexplicably small amount for Propane is not able to take away the impression that for these saturate hydrocarbons the volume increases regularly and equally whenever 1 atom of C and 2 atoms of H enter the molecule, and when we consider the almost perfect equality of $\frac{T_k}{p_k}$ for Pentane and Isopentane, we come to the conclusion that at least in these cases a rearrangement of the atoms is no influence of importance. If for the mean of the above values (with the exclusion of 2,37) 2,76 is chosen, the volumes would be as the calculated values of the preceding table indicate. It is seen that except for Propane, the differences are small, and the question suggests itself whether for this substance there is a cause of error in the determination of the critical quantities, e.g. a certain degree of impurity.

If in what follows the volume of the carbon atom is represented by C, and the volume of the hydrogen atom by H, we have the following two equations for the determination of these two quantities:

$$C + 4\,H = 3{,}483$$
$$C + 2\,H = 2{,}76\ ^{1)}$$

or $H = \frac{0{,}723}{2} = 0{,}3615$ and $C = 2{,}037$.

Some other determinations which will be discussed presently, have led me to consider C below 2 as possible. With $C = 1{,}9$, retaining $CH_4 = 3{,}483$, H would be equal to 0,396. Then CH_2 would have fallen to 2,691, so it has changed only little. But whether one assumes $H = 0{,}3615$ or $H = 0{,}396$, it appears that there is a great difference with the volume of H or H_2 as it would follow from the critical data of hydrogen. With $T_k = 32$ and $p_k = 19{,}4$ we find $\frac{T_k}{p_k} = 1{,}65$. And if we should assume the formula H_2 for the molecule as I also did at first, $H = 0{,}825$ would follow from this, a value which is certainly not in harmony with the above calculated value. And the difference is so great that I was already again on the verge of concluding, as I had often supposed before, that it would be impossible to get in this way to the knowledge of the size of the

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1) From methylethylethylene(iso) which, the structure being disregarded, has $C_5H_{10} = 5\,(CH_2)$ as formula, we find $\frac{T_k}{p_k} = 13{,}69$, which would lead to $CH_2 = 2{,}738$. But from ethylene, which has 2 (CH_2) as formula, we should find a somewhat too great value, viz.: $2\,(CH_2) = 5{,}7$ or $CH_2 = 2{,}85$. Is this substance somewhat associating?

atoms. Now however I bethought myself that I had determined the size of the hydrogen molecule already before, and that this size was even the first molecule size that I had at least estimated. From REGNAULT's observations, in which the volume under 1 meter pressure was assumed as unity of volume, I had obtained values lying between 0,0005 and 0,0008, which for our unity of volume corresponds to 0,00038, and 0,00006, from which for $\frac{T_k}{p_k}$ a value would follow lying between 0,95 and 1,5. And a value lying near 0,95 seems by far more probable to me than the value which would follow from the critical data, and leads me to conclude that at these low temperatures hydrogen associates to double molecules for the greater part.

But nevertheless the value of the volume of the atom H remains decidedly smaller when it is bound to $^1/_4$ part of the atom C, than when it is bound to a second atom H. And this is a result which has always appeared correct to me, viz. that the size of the volume of an atom is not only determined by its own nature, but also by the nature of the atom to which it is bound. This is of course in flat contradiction with the assumption that an atom is a perfectly invariable corpuscle, not to be changed by any forces, not by *atomic forces* either. With the molecules as wholes it must, indeed, have the property in common of being invariable to forces of collision of heat and of pressure. But when uniting with other atoms, in which forces of higher order come into play, they behave, I would almost say, as soft bodies, which can vary both with regard to shape and to size. And the conception that an atom is an orbit of electrons round a rigid centre formed by a point in which the atomic weight is concentrated, or when the atom is bi-, tri- or tetravalent by 2, 3 or 4 orbits round centres in which $\frac{1}{2}, \frac{1}{3}$ or $\frac{1}{4}$ of the atomic weight is concentrated — a conception called into existence by the study of light phenomena [1]) — can give an explanation of this. We have only to assume the velocity in the orbits large with respect to the velocity of the thermal motion to account for the apparent hardness, and only to assume rotation of the molecules round one or more axes to convert orbits and planes to an apparent volume. When we have two similar atoms which have united, we have two orbits of electrons lying in the same plane, and rotating in opposite direction. Where they are in contact or almost in contact, the directions are in the same sense, hence we have

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[1]) Cf. among others Dr. BOHR, Phil. Mag. 1913.

attraction, just as this is the case with electric currents in the same direction. But when one of the atoms is replaced by one of another nature, e.g. of greater atomic weight, the size of the atom that has not been replaced, changes, because a stronger current acts on it, i. e. this atom becomes smaller, whereas the second atom becomes larger than it would be if it had continued to be united with one of its own nature, and the result can be that the new molecule is either greater, or smaller than, or has happened to remain equal to half the volumes of the two molecules, the atoms of which have been exchanged. But we do not yet know the degree of the variability.

But let us after these speculative considerations return to the investigation whether also other observations about the critical circumstances are in agreement with the values of C and H, which we have calculated above for the case of mutual binding.

It had already drawn my attention that $\frac{T_k}{p_k}$ for isopentane had been found somewhat smaller than for normal pentane, and that, if this should also be the case for other iso-compounds, the earlier calculations, in which these differences were not found, could not be quite accurate. And strictly speaking already in the earlier calculation it can be pointed out that there are differences which have been neglected in this calculation. The volume for all atoms C e.g. was put equal, though there always exist 2, viz. the outmost of the chain, which are bound to 3 atoms H and 1 atom C, whereas there are $n-2$ atoms C, which are bound to 2 atoms H and 2 atoms C, and which will accordingly be smaller than the 2 outmost. For the iso-compounds the case may even present itself that an atom is bound to 1 atom of H and 3 atoms of C, and perhaps even that one atom of C would be bound to 4 atoms of C. I was therefore glad that for a few iso-compounds the quantities T_k and p_k are determined through investigations by SYDNEY YOUNG — viz. for di-isopropyl and di-isobutyl. For the former substance, for which, if the construction is disregarded, the composition is the same as that of Hexane, $\frac{T_k}{p_k} = 16.3$, and for the latter, the composition of which would be equal to that of Octane, $\frac{T_k}{p_k}$ is equal to 22.4. For normal compounds the values are 17,06 and 23,1 in the above list. Also for these compounds the case occurs that the volume is smaller than for normal ones, and even not inconsiderably.

But on account of the incertainties as to in what way and to what degree the differences in size of the volume of the different C atoms would have to be taken into account, I shall not attempt as yet to calculate the found differences in size, at least not for the present. For isobutyl, moreover, the difference in size amounts only to 3 percent, and it always remains the question how far the accuracy of the determination of T_k and p_k has been carried, and in how far the absolute purity of the substance and the equality of the factor $\frac{7 \times 273}{(1 + a)(1-(q}$ can be relied on. I shall therefore for the present be satisfied with the approximative calculations, which I have used above.

For the methyl-, ethyl-, propyl-compounds etc. there is a whole series of determinations of T_k and p_k which can be of use for the calculation of CH_2. Then a new kind of atom, or a new group of atoms, which we do not know as yet, is indeed added, but when the new group of atoms is bound in these compounds in the same way, the difference in $\frac{T_k}{p_k}$, e.g. for the methyl- and ethyl-series, can then enable us to determine the value of CH_2. Thus we find the following values:

	T_k	p_k	$\frac{T_k}{p_k}$	CH_2
Methyloxide	127,1 + 273	53	7,55	$\frac{5,57}{2} = 2.78$
Ethyloxide	193,8 + 273	35,6	13,12	
Methyl and ethyloxide	167,6 + 273	46,27	9,5	

The value 2.78 coming so near the previous determination, I do not hesitate to call the value $\frac{T_k}{p_k}$ for the third substance too small. There the value 10.25 is to be expected instead of 9.5. If one should assign the before given value also to the other H and C atoms, $O = 1,3$ would follow from this, whereas $O_2 = 3$ follows from $\frac{T_k}{p_k}$.

Thus we find for:

	$\frac{T_k}{p_k}$	difference
Methylacetate	10,95	
Ethylacetate	13,77	2,82
Propylacetate	16,56	5,61

From this we should therefore derive $CH_2 = 2,8$. So the abnormality of acetic acid has disappeared in these compounds; of these compounds and others examined by me the group CO_2 would almost give the value which follows from T_k and p_k for CO_2, viz. 4,14.

I choose three of the compounds of Cl, and C and H to see in how far the others by means of the values calculated from these, can be derived.

From the values of T_k and p_k follows:

Chloric ethyl	C_2H_5Cl	$= 8,435$
and	$C_2H_4Cl_2$	$= 10,61$
and	$CHCl_3$	$= 10.$

We find from this $Cl—H = 2,175$, which means that if in these compounds a hydrogen atom is substituted for the chlorine atom, the volume increases by 2,175, a value which was found equal to from 2,18 to 2,2 another time; a second equation is:

$$Cl_4—H_2 = 9.39.$$

From these two equations follows $Cl = 2,52$ and $H = 0,345$ and we find further $C = 2,095$, a value almost equal to that found before. For carbon tetrachloride we find 12,175 for $\frac{T_k}{p_k}$ with these calculated values of Cl, H, and C, whereas the value found directly would be equal to 12.4. But for $CClH_3$ there is no sufficient agreement between observation and calculation, and like other substances which have been derived from CH_4 this substance yields a too large value and is evidently associating. I am even astonished that the derivatives that contain more chlorine behave evidently so normally. When we compare the value found for Cl with that of the molecule, viz. 4,48, it appears that the binding of C with Cl makes the atom Cl larger than is the case with the binding of Cl with Cl. With the values calculated from chlorine compounds we should find:

$$CH_4 = 3.475$$
$$CH_2 = 2.785$$

When these are compared with those found before:

$$CH_2 = 3.483$$

and $$CH_2 = 2.76$$

there is reason for us to wonder that the entering of Cl into these compounds hardly changes the values of C and H, if at all.

I shall now proceed to the amine compounds.

We find for the ethyl amine compounds the values of $\frac{T_k}{p_k}$:

tri-ethylamine di-ethylamine and ethylamine
17.7 12.25 6.818

When the volume of C bound to N is represented by C_N and that of C bound to C by C_c, we have the three following equations:

$$N + 3\,(C_N + H_2 + C_c + H_3) = 17.73$$
$$N + H + 2\,(C_N + H_2 + C_c + H_3) = 12.25$$
$$N + 2\,H + (C_N + H_2 + C_c + H_3) = 6.818$$

or

$$-\,H + (C_N + H_2 + C_c + H_3) = 5.483$$
$$-\,2\,H + 2\,(C_N + H_2 + C_c + H_2) = 10.915$$

and so

$$C_N + H_2 + C_c + H_2 = 5.483 \text{ of } 5.457.$$

If we take the mean of these values, and if we take into consideration that for $C_c + 2\,H$ has been found before 2.76, we determine:

$$C_N + 2\,H = 2.71.$$

Hence the volume of C bound to N may be equated to that of C bound to C.

If we do so, and calculate with it the value of the group (NH_3), the radical of the amine-compounds, we find:

$$(NH_3) = 1.3 \text{ about.}$$

This value is much smaller than for NH_3, which we call ammonia. With $T = 132.3$ and $p_k = 109.6$ we calculate this value at about 3.7. So there the question rises what difference there will be between these two atom-groups. Perhaps it will have to be looked for in the situation of the orbits of the electrons, which would then have to lie in the equator plane of the trivalent nitrogen atom for ammonia, and for amine in the meridian plane.

For propylamine we should find a slightly too high value, viz. 2.84, for the value of CH_2 from $\frac{T_k}{p_k}$ with $(NH_3) = 1.3$, whereas we found a somewhat too small value before for propane. I do not, therefore, consider these differences as really existing. For dipropylamine the value $1{,}3 + 16{,}56 = 17.86$ might be calculated with $1.3 + 6CH_2$, whereas 17.47 follows from $\frac{T_k}{p_k}$. Allowing for the approximate character of our equations this may be considered as equal.

But the methylamines all yield a too high value, which I consider as a consequence of association, viz. 10.575 instead of 9.58, 7.43 instead of 6.82, and 5.944 instead of 4.06. With monomethylamine there is, therefore, a high degree of association; about half the molecules are double molecules.

I shall now proceed to discuss the substances in which the cyclic bond of benzene occurs.

For benzene itself we find $\frac{T_k}{p_k} = 11{,}73$, and for all the substances in which this cyclic bond occurs, C_6H_6 is smaller than would follow from the saturate hydrocarbons. Of the substances in which the grouping of C and H occurs, as this is the case for hydrocarbons, 6 C alone would already have a value exceeding 12 or close to it. So the question again rises for what special reasons the cyclic bond of the 6 carbon atoms makes them smaller. Perhaps the closed chain, the ends of which coincide, is the cause of this through the mutual attraction of these ends.

That the binding of C to C with 3 valencies could account for this, may be doubted for the present.

But whatever the cause may be — we shall assume $C_6H_6 = 11{,}73$ for the cyclic binding, and take the former value for the atoms further entering the molecule, which are grouped as in the saturate hydrocarbons.

For diphenyl we find $\frac{T_k}{p_k} = 24{,}17$; it is, compared with benzene, a little too great, or perhaps benzene is a little too small. By adding 2,76 to diphenyl we should get 26,93 for diphenyl methane whereas 27,3 would follow from $\frac{T_k}{p_k}$. Whether these differences are the consequence of our *approximate* calculation, or whether they have a real signification, I dare not decide. By the addition of CH_2 to benzene $11{,}73 + 2{,}76 = 14{,}49$ follows for toluine, whereas $\frac{T_k}{p_k}$ yields 14,27.

We find further:

Xylene (o)	for $\frac{T_k}{p_k}$ the value	17,1,	calculated from benzene	17,25
,, (m)	,, ,, ,, ,,	17,64,	,, ,, ,,	
,, (p)	,, ,, ,, ,,	17,28,	,, ,, ,,	
Mesitylene	for $\frac{T_k}{p_k}$ the value	19,3 ,	calculated from benzene	20,01
Durene	,, ,, ,, ,,	23,62,	,, ,, ,,	22,77
Cumene	,, ,, ,, ,,	19,74,	,, ,, ,,	20,01
Cymene	,, ,, ,, ,,	22,78,	,, ,, ,,	22,77

From Cresol (O) $= 15{,}67$ follows for $-H + (O,H)$ the value 1,17. If the two H cancel each other, we should have $O = 1{,}17$, whereas we calculated $O = 1{,}3$ from the ethyl-oxides. If we had a priori assumed $O = 1.3$, we should have calculated Cresol $= 15{,}79$.

I might add other examples to these, but those given here suffice in my opinion to draw the following conclusions:

1. The volume of the molecules of normal substances may be found from the critical circumstances.
2. The volume of the molecules is equal to the sum of the volumes of the atoms contained in it.
3. The volume of an atom is not constant, but depends also on the atoms to which it is bound, and the way in which it is bound to others.
4. By normal substances we understand such as do not associate or dissociate. For acetic acid 10.415 is found for $\frac{T_k}{p_k}$ whereas $C_2H_4O_2$ would lead to 7,823 at the most.
5. The view that the volume of an atom is determined by the size of the orbits of the electrons holds out the prospect to determine the modification of the size in case of mutual binding.

I had just commenced this investigation on the size of b, when I received the copies of nine treatises by ALBERT P. MATHEWS on the value of a, in which very remarkable results have been obtained. They appeared in the "Journal of Physical Chemistry" of 1913.

APPENDIX.

The comparison of Benzene with Naphthaline has given me the conviction that the smallness of C_6H_6, as was indeed to be expected, must not be ascribed to the H-atoms, but to the C-atoms. For naphthaline $\frac{T_k}{p_k}$ is equal to 18.91. Now naphthaline is equal to twice $\frac{2}{3}$ benzene $+ 2$ C or $\frac{5}{3}$ benzene 2 H. We have, therefore, the equations:

$$18.91 = \frac{4}{3} \times 11.73 + 2C$$

and

$$18.91 = \frac{5}{3} \times 11.73 - 2H$$

or

$$18.91 = 15.64 + 2C$$

and

$$18.91 = 19.55 - 2H,$$

from which $C = 1.635$ and $H = 0.32$ is calculated. The value of H is of the former order of magnitude. But C has decreased to 0.8 of its former value. This appears still more clearly when benzene is compared with hexamethylene or cyclohexane. With this latter substance we have also the cyclic binding of 6 carbon atoms; only the coincidence of two valencies for carbon has disappeared. The formula is C_6H_{12} and $\frac{T_k}{p_k} = 13.9$. Hence the comparison with benzene gives the two following equations:

$$6\,C + 12\,H = 13.9$$

and

$$6\,C + 6\,H = 11.73$$

or

$$H = 0.3616$$

and

$$C = 1.593$$

I will still give a few values calculated in the meantime, viz. propylbenzene, calculated with benzene and $CH_2 = 2.76$, equal to 20.01, $\frac{T_k}{p_k}$ being equal to 19.772, and chlorobenzene with $Cl—H = 2.185$ calculated at 13.915 and found 14.18.

But all the nitriles appear to give much too high values of $\frac{T_k}{p_k}$, and so for b, and are associating in a high degree. Even benzonitril, but this nitril in a less degree than the others.

Astronomy. — "*Investigation of the inequalities of approximately monthly period in the longitude of the moon according to the meridian observations at Greenwich*". *Addendum*. By J. E. de Vos van Steenwijk. (Communicated by Prof. E. F. v. d. Sande Bakhuyzen).

Professor Battermann and Prof. Ernest Brown have both been so kind as to point out to me, in letters to Prof. Bakhuyzen, that Brown's theoretical value, quoted by me, for the motion of the moon's perigee (p. 140), which was taken from *Monthl. Not.* **64** 532, does not quite agree with his final result, which was published by him in *Memoirs R. A. S.* **59**, 94 (comp. also *Monthl. Not.* **70**, 3). If we use the value assumed by me for the ellipticity of the earth 1 : 297.5, then the theoretical result for the sidereal motion in a Julian year for 1850 becomes **146435″16**, so that my result from the observations **146435″31** is now only 0″15 greater, against 0″26 formerly.

We approach, therefore, the limits within which this difference might be ascribed to the errors of observation. However, I now think, that the difference which was found, small as it is, still deserves closer consideration, and this especially with regard to the value which NEWCOMB has deduced for this motion from the long series of observed occultations discussed by him in his lately published posthumous paper *Researches on the motion of the moon.* He found (p. 225) **146435″29 ± 0″02**, a result which appears to be very accurate and which agrees almost exactly with mine.

This induced me to consider in how far the small difference might be ascribed to inaccuracies in the values, deduced from observations, on which the theoretical calculations are founded. Such inaccuracies might occur in those parts of the motion of the perigee which depend upon the figure of the earth and of the moon. The latter part is very small, but probably also very uncertain. It must be calculated from the libration-phenomena and BROWN deduced for it, from HAYN's results, 0″03.

Much greater (6″4) is the influence of the ellipticity of the earth, or more exactly of the difference between its polar and equatorial moment of inertia, which can be deduced both from the results of gravity determinations and from measured terrestrial arcs, by means of relations that are connected with CLAIRAUT's theorem. However, these deductions are open to criticism, as BATTERMANN also pointed out. Still we see that, when the ellipticity of the earth is calculated from the most reliable results, recently deduced from both classes of observations the results agree well with each other, and this makes it appear probable, that also the values deduced for the difference of the moments of inertia and thereby for the constant of the lunar perturbations would be fairly accurate.

From the gravity determinations HELMERT deduced 1 : 298.3 a few years ago, and recently HAYFORD and BOWIE deduced from determinations in the United States 1 : 298.4 [1]). On the other hand, HAYFORD, from his discussion of all the measured arcs in the United States found 1 : 297.0, while in Europe, from the Russio-Scandinavian arc of meridian, 1 : 298.6 was deduced. In the American calculations reductions for isostatic compensation were applied.

According to these results the value adopted by me 1 : 297.5 would appear to be too large rather than too small. But now it is remarkable, that all lunar perturbations which are caused by the

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[1]) A division of the 89 stations into 2 groups, an eastern and a western, led to 1 : 297.8 and 1 : 299.6 respectively; the addition to the 89 stations of 10 stations in Alaska gave, however, as the result from all 1 : 300.4.

figure of the earth would indicate a greater value for the ellipticity. Amongst these perturbations there are four which have a somewhat considerable coefficient:

1. a motion of the perigee;
2. a motion of the nodes;
3. a periodic inequality in the longitude;
4. a periodic inequality in the latitude.

The first of these, according to our results, would lead to 1 : 294.3, according to NEWCOMB's to 1 : 294.6; the second, according to NEWCOMB's results, would yield 1 : 294.3 and the 4th, according to NEWCOMB, 1 : 293.7, while the 3rd which has a period of 18 years cannot be used for our purpose on account of the unexplained inequalities of long period in the mean longitude. Are these differences to be regarded as real and would therefore the measurements made on the surface of the earth not lead to an accurate determination of the difference in the moments of inertia?

On account of the possibility that other circumstances may exercise an influence upon the motions of the perigee and node, the periodic inequality in the latitude, which has a monthly period, would certainly be the most likely to yield a decisive answer to this question, if it were not that an error in the assumed obliquity of the ecliptic has precisely the same influence upon the declination of the moon as the inequality in the latitude. (See also NEWCOMB's very interesting Addendum to Chapter XI, p. 226).

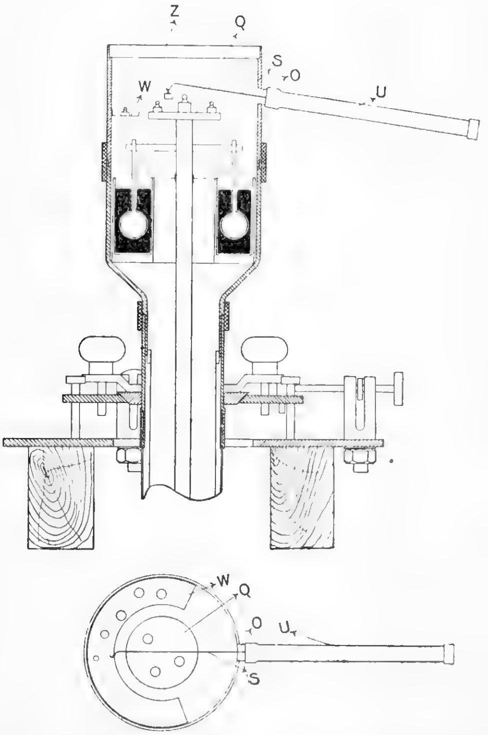
Physics. — "*Magnetic researches.* XI. *Modification in the cryomagnetic apparatus of* KAMERLINGH ONNES *and* PERRIER." By Dr. E. OOSTERHUIS. Communication N°. 139*b* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 31, 1914.)

In the researches on paramagnetism at low temperatures, described in N^{os}. VI, VII, and VIII of this series (Comm. N°. 129^b, 132^e, 134^d), an apparatus was used, in the main the same as that constructed by KAMERLINGH ONNES and PERRIER, of which a complete description is found in Comm. N°. 139^a.

In one particular, however, a change was made in the apparatus. The apparatus so changed, which was briefly indicated in § 1 of Comm. N°. 129^b, is here more fully described. The force acting upon the experimental substance in the tube, when it is placed in an inhomogeneous magnetic field, was measured in Kamerlingh Onnes and Perrier's apparatus by electro-magnetic compensation. This can be replaced with advantage by a compensation by means of weights, an opportunity for which is given by the scale Q placed upon the carrier ¹).

The hook S serves to move the weights on and off the scale, while the apparatus remains air-tight; it can be moved from the outside, through the opening O. The rubber tube U is hermetically attached to the rim of the opening O, and also to the extremity of the hook; in this way, the tube and the hook together can be moved sufficiently ²) to be able to lift the weights from the wall table W and place them on the scale, or vice versâ. The glass plate Z enables these manipulations to be watched from the outside. To prevent the rubber tube collapsing when there is a partial vacuum in the apparatus, it is supported on the inside by a flexible spiral of steel wire. We further refer to the figures, in which the upper portion of the apparatus,



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¹) In the apparatus described in Comm. N⁰. 139a there was also a scale fixed at the top of the carrier; the weights placed upon it did not however serve to measure the force, but only to obtain an approximate equilibrium against the upward pressure of the liquid. (See § 3^d Comm. N⁰. 139a).

²) Compare the similar arrangement for stirring in cryostats, Comm. N . 83 § 4.

as it appears after our modification, is shown in section and seen from above. The lower part remained unchanged [1]).

The arrangement here described has some advantages over that with the electro-magnetic compensation. In the first place, a much greater force S can be measured by it, and moreover the method of working is simpler, as now only one current (that of the electro-magnet) has to be read, in the earlier arrangement three. On the other hand, while in the former arrangement the current through the electro-magnet was adjusted to certain fixed values, for which the corresponding strengths of field were accurately measured, in the modified arrangement it is best to place a certain weight upon the scale, and to regulate the current through the electro-magnet, until this weight is exactly compensated by the force exerted upon the experimental substance by the magnetic field. As the strength of field corresponding to this current must now be found by (graphic) interpolation, it can now only be as accurately known as by the method described in Comm. N°. 139^a, if the field has been determined for a great number of current strengths. Naturally in the method of compensation by weights we could also work with a few accurately measured magnetic fields, if we had a sufficient number of small weights at our disposal inside the apparatus; but working in this way would greatly decrease the simplicity of the method. For this reason in these investigations by the method of compensation with weights, the field for the WEISS electro-magnet for different strengths of current, was very minutely studied.

Physics. — "*Magnetic researches.* XII. *The susceptibility of solid oxygen in two forms*". By ALBERT PERRIER *and* H. KAMERLINGH ONNES. Communication N° 139*c* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of January 31, 1914.)

§ 1. *Introduction.* A former investigation [2]) had led us to the conclusion that the susceptibility of oxygen suddenly becomes considerably smaller when this substance changes into the solid state.

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[1]) The sectional drawing of the upper portion of the apparatus is drawn on the same scale as the fig. in Comm. N°. 139*a*, and gives therefore, if placed upon that, the complete drawing of the apparatus as used in the researches of Comm. N°. 129*b*, 132*e* and 134*d*.

[2]) H. KAMERLINGH ONNES and ALBERT PERRIER, Leiden Comm. N°. 116 and 124*a*.

How great the jump might be, was uncertain, owing to the absence of a bath which would keep the temperature constant at which this change takes place. We were therefore obliged to draw our conclusions from what we observed during a gradual heating, at which the temperature can be only imperfectly estimated. A further investigation was therefore necessary. Moreover, in repeating our determinations, we encountered the difficulty, that we found a different value for the susceptibility of solid oxygen at the temperature of liquid hydrogen, than in our first experiments, which were conducted according to a different method. Although we thought we were justified (Comm. N°. 124) in considering that we had obtained reliable results only by the second method, and that in the meantime we need not attach any value to those obtained previously, it was still very desirable to confirm the more recent value for the jump by new measurements. Finally, in our experiments we came upon another problem that required to be solved. We had noticed (see Comm N°. 122*a* May 1911) as WAHL[1]) also observed later, that solid oxygen, besides appearing in the blue-grey opaque form that it usually presents, also occurs in a transparent vitreous form. This modification can optically be very clearly distinguished from the liquid state. We conjectured that the transition from the transparent condition to the other one might be accompanied by a second jump in the magnetic condition, following on that which took place on freezing. We wished to ascertain the truth of this also.

§ 2. *Arrangement of the experiments.* For the magnetic determinations, as in previous investigations, we made use of the method of measuring the attraction which the magnetic field exerts upon a rod of the experimental substance placed at right angles to the field in the interferrum of an electro-magnet, and held suspended there by a carrier with hydrometer-arrangement.

More specially the arrangement of the apparatus was in the main the same as that used for our investigations of the liquid mixtures of oxygen and nitrogen, of which we shall give a complete description in the next paper (Comm. N°. 139*d*). We do not give it here, because the investigation treated in this paper, is of a much more preliminary character than our investigation of mixtures, confining ourselves here in the main to that which is peculiar to our experiments on solid oxygen. At the outset it should be mentioned that the way in which the temporary connection was made between the carrier

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[1]) Zeitschrift für physikal. Chemie. Bd. 84 (1913).

and the apparatus which introduced the oxygen from outside, was the same as in the experiments with mixtures of oxygen and nitrogen.

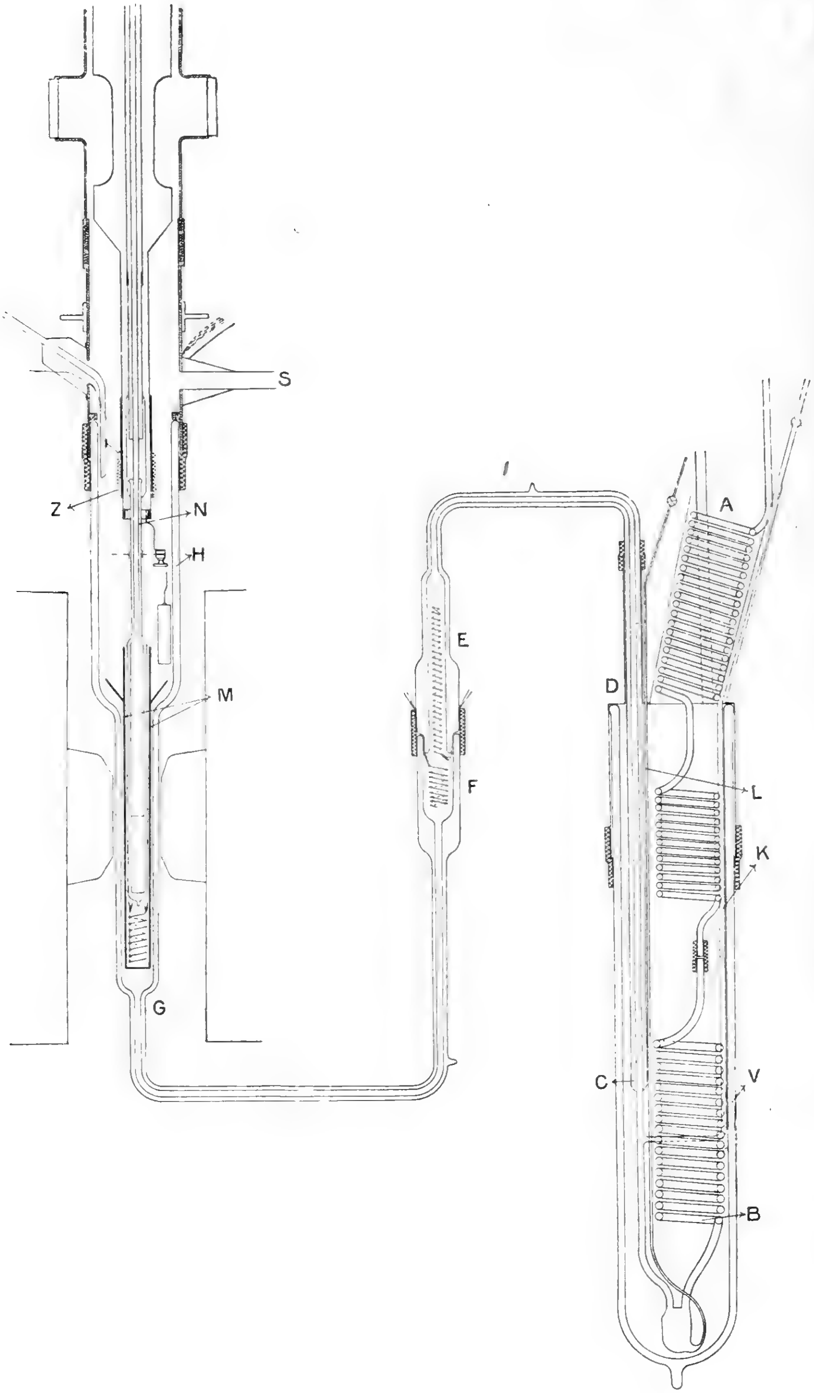

Fig. 1.

In the further description we shall assume that the drawing of the apparatus as it is given in this paper will be consulted as a modification together with that of the next paper (N°. 139*d*). The development of the apparatus there described, from our original apparatus and the modification due to OOSTERHUIS (Comm. N°. 139*b*) will be obvious on comparison with Comm. N°. 139*a*.

In the cryogenic part, we encountered in the first place a difficulty, which so far had not been provided for. Measurements had to be made at the temperatures between the melting-point of oxygen and the boiling-point of hydrogen, as well as at the temperatures of liquid and solid hydrogen. In order to be able to do this an arrangement was made which permitted us to work both in a bath of liquid hydrogen evaporating under various pressures, and in a bath of hydrogen gas, the temperature of which can be regulated.

The arrangement consists principally in a circulation of hydrogen. The hydrogen, after having been cooled to the boiling point, before it comes in contact with the experimental object, passes over a heating-spiral, in which JOULE heat is generated, and is thereby heated to the desired temperature. The whole hydrogen circulation is carefully shut off from the outside air. The gas streams from a supply-cylinder in which it is kept under pressure, through a copper spiral AB, the glass tube CDL, which from CE is double-walled, and silvered, and at E is widened, to the experimental space in the cryostat. It enters this through the twice bent double-walled tube FG, which forms the downward continuation of the vacuum-vessel of the cryostat. On the way down the gas is cooled by liquid air at A (copper spiral), and is further cooled first by hydrogen vapour and then by liquid hydrogen at B (glass spiral). At E the gas passes along a resistance thermometer; at F is the heating wire, at G in the lower part of the experimental space a resistance thermometer.

By means of regulating resistances the current through the heating wires is so regulated as to obtain the desired temperature in the experimental space. In the upper part of this there is a helium thermometer with a steel capillary, which forms part of our cryomagnetic apparatus in its usual form (Comm. N°. 139*a*). The gas then rises further in the vacuum-vessel, and escapes through S into the gasometer or the air-pump. The tubes K and L serve for leading off hydrogen.

Of the various auxiliary apparatus we must further mention the thick-walled copper tube M, which surrounds the experimental tube, and which serves to keep the temperature of the gas which surrounds it even all over. Of course liquid hydrogen can be introduced into the cryostat in the ordinary way, to immerse the experimental tube in a bath of liquid hydrogen.

We had a good deal of difficulty in procuring a rod of solid oxygen of about 5 or 6 cm. length that was *completely homogeneous*. As in freezing the volume of the oxygen diminishes by about $^1/_9$ there is a great tendency to form hollows. A homogeneous rod can only be obtained by allowing the liquid in the cylindrical mould to gradually freeze *from the bottom upwards*. As soon as solid matter settles in the neck of the tube, hollows must arise in the experimental mass, as the entrance of liquid oxygen is cut off [1]). The difficulty of procuring an homogeneous cylinder was increased by the fact that in our experiments the freezing had to take place inside a silvered vacuum glass, and could therefore not be followed by the eye.

In order to come a step nearer to the solution of this problem, which still presents difficulties, we made use of the possibility of regulating at pleasure the heat conducting power of a double-walled vacuum glass. The experimental tube in which the oxygen was frozen was made double-walled (not silvered): as much hydrogen was put in between the walls that the (small) pressure had exactly such a value, that according to preliminary experiments in a transparent bath the freezing took place under the most favourable circumstances. It appeared to be favourable to this that in the upper part of the tube latent heat was developed by the condensation of the gaseous oxygen which was admitted during the freezing. When a once formed stick partially melted, it was difficult to get it back into a dense condition. The double wall of the experimental tube is therefore also of use to eliminate temporary irregularities in the temperature of the surrounding bath (vapour or liquid). It was found that the temperature-range of the transparent modification did not extend more than 5 or 6 degrees below the melting point.

§ 3. *Results.* The figures in the following table are averages. To be able to express the results in absolute measure, the fields are measured in absolute measure, and the dimensions of the tubes carefully determined. The tubes were of the symmetrical type (see Comm. N°. 139*a* § 4), the lower part was evacuated, so that no

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[1]) We shall return later to the freezing of oxygen and the change from the transparent to the opaque mass. When the access of gaseous oxygen is cut off, a long shaped hollow usually forms which as it increases assumes the shape of a worm fantastically coiled up in a confined space.

correction was needed for the magnetism of the bath or of the wall. The oxygen used contained not more than 0,001 foreign admixtures. The immediate result of the observations is the susceptibility K per unit of volume; to calculate the value of χ, the specific susceptibility (or specific magnetisation coefficient), we must know the density ϱ. We have taken 1.44 for this, on the ground of our determinations in 1910, and from a new one recently made, but neither determination can lay claim to great accuracy, so that the values of χ (and also of K for the opaque modification if it should prove that in this innumerable little splits are present) will have to be recalculated when ϱ is better known.

The four results refer to one freezing.

TABLE I.

Susceptibility of solid oxygen.

bath	T	$K . 10^6$	$\chi . 10^6$ ($\varrho=1.44$)
H_2 vap.	43	166.1	115.3
H_2 liq.	20.3	79.	54.9
	17.3	77.3	53.7
	13.9	76.7	53.3

A new freezing gave two values for K near $165.5 . 10^{-6}$ (before and after partial melting) at about the same temperature (—230° C.). This value is less to be relied upon than that in the Table. We had very little time at our disposal for our joint work, and this was even diminished by the apparatus being found somewhat deficient in some points. On this account we had not time to test a temperature lying between the melting point and the transition point from the transparent to the opaque modification. But we had already postponed the resumption of our researches after the departure of one of us from Leiden, for two years, and we shall not have an opportunity in the near future to continue our joint research. We therefore felt bound to publish what we had so far established.

This is, besides the numerical values of our table within the limits of accuracy given for it, that the transition from the transparent modification of oxygen to the opaque, which takes place at about − 225° C., *is not accompanied by any conspicuous magnetic modification,* so that it probably does not involve any important change in molecular structure. Further, that in the whole range from the freezing point of oxygen down to about — 240° C. the susceptibility is markedly less than in the liquid state. In this region it changes little with the temperature, in fact increases slightly on cooling. This does not seem to agree with the much smaller value which the table gives for — 253° C. but here a phenomenon intervenes which has not been observed before, viz. that at about — 240° C. the *susceptibility suddenly falls to about half its value.* The exact value of the temperature must still be more accurately determined; it is also not settled whether the transition is actually discontinuous or is completed in a very small range of temperature (1 or 2 degrees). The susceptibility falls in this transition to about the values that are found in liquid hydrogen.

It will be seen that these last values agree with the values of 1911, within the limits of accuracy of the latter. The results of 1910 are thereby, as we expected, condemned, and the cause to which we attributed the discrepancy between these results and those of 1910, gains in probability at the same time.

As regards the change in the susceptibility below — 252° C. with the temperature, although it is slight, yet it allows no doubt that it is a decrease. The observations permit the comparison of the susceptibility at different temperatures at constant density without the intervention of any correction. We have here, therefore, a new example of a substance that follows Curie's law at a higher temperature, and on approaching the absolute zero completely deviates from it. As the ratio of the susceptibilities observed above and below the transformation point is

$$\lambda_1 = \frac{115.3}{54.2} = 2.10,$$

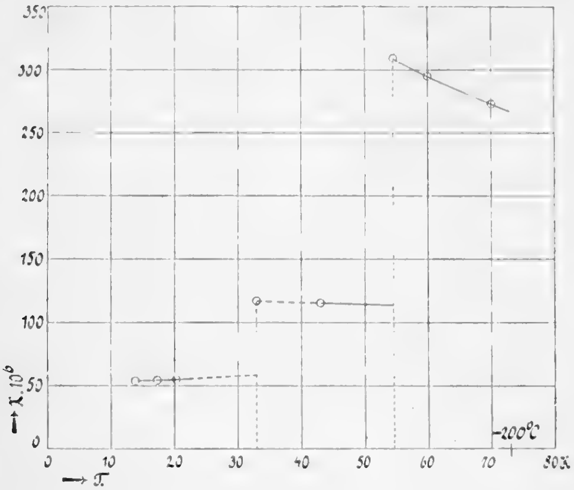
it becomes probable that the exact value of the jump is precisely 2. For above 20° K, the magnetisation must still increase distinctly.

For the ratio of the susceptibility of liquid oxygen and solid oxygen at — 230° C. we find

$$\lambda_2 = \frac{313.3}{115.3} = 2.72\,.$$

This value is less certain than that of λ_1, for it contains the uncertainty concerning the density of solid oxygen and that of the change of susceptibility between — 220° C. and — 230° C.

From our previous investigations we had inferred a sudden change in the susceptibility to a fifth or sixth part of its value between the liquid state and the solid state at hydrogen temperatures. It now appears that a sudden change of this amount really exists, but takes place in two parts, namely, once to $^1/_2$ at freezing, and subsequently,



Fig, 2.

after the susceptibility has again increased a second time to $\frac{1}{2}$ at the transformation point — 240° C., after which the susceptibility further decreases. In the accompanying figure our results are put together.

Physics. — "*Magnetic researches* XIII. *The susceptibility of liquid mixtures of oxygen and nitrogen, and the influence of the mutual distance of the molecules upon paramagnetism.*" By Albert Perrier and H. Kamerlingh Onnes. Communication N°. 139*d* from the Physical Laboratory at Leiden. (Communicated by Prof. H. Kamerlingh Onnes.)

(Communicated in the meeting of January 31, 1914).

§ 1. *Introduction.* In 1910 and 1911 we published experiments upon the susceptibility of oxygen at very low temperatures, by which it was demonstrated that the specific susceptibility of this substance, which, in the gaseous form above 0° C. follows Curie-Langevin's law, deviates considerably from this law in the liquid state at low temperatures, and even more so in the solid state.

Subsequently we have observed similar phenomena in other substances (paramagnetic salts). The (solid) substances referred to follow Curie's law at ordinary temperature, and also at temperatures that do not lie too far below it; but when the temperature falls to the neighbourhood of the boiling point or the freezing point of hydrogen, they deviate from the law *in various degrees*[1]), *but always in the direction of decrease of the susceptibility.*

We think it advisable to recall here in a few words some of the views and hypotheses which guided us in the above-mentioned researches, in order to make clear the connection of the former experiments to each other, and to the determinations we shall here deal with, and to elucidate the object of these last.

When we began our magnetic investigations at low temperature (in 1908) we wished, amongst other things, to test LANGEVIN's recently published theory of paramagnetism which leads to CURIE's law, at low temperatures.

On this account (and on others, see Comm. N°. 116, § 1) it was natural we should begin with oxygen. The deviations that we found in oxygen together with what we observed in other substances, gave us ground to suppose phenomenologically that there would be a law of corresponding conditions for the deviations from CURIE's law. This again gave rise to the question of how LANGEVIN's theory would have to be supplemented in view of the new phenomena. Our first idea was the possibility of polymerisation, which might take the form of association in oxygen. As the degree of association of liquid oxygen if diluted with a non-active substance, would be changed, and as diamagnetic nitrogen could serve as such a substance, we thought (see Comm. N°. 116, § 5) that by experiments on mixtures with this substance we should be able to ascertain whether it was a case of polymerisation or not.

An experiment made with a less satisfactory apparatus than that which we now use, gave an indecisive result, and even led us to a wrong conclusion, as it seemed to support our assumption of the same change with temperature in the specific susceptibility of oxygen independent of the distance that separated the molecules from each other. In other words it still appeared possible to us that the specific susceptibility of oxygen vapour at the boiling-point might be the same as that of liquid oxygen, and that therefore gaseous oxygen at this temperature would deviate from CURIE's law to the same extent as liquid oxygen. Our intention soon to make further measurements on mixtures of oxygen and nitrogen, came to nothing, as one of us left Leiden. It was a considerable time before we were able to continue our experiments.

In the mean time, KAMERLINGH ONNES and OOSTERHUIS's investiga-

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[1]) KAMERLINGH ONNES and PERRIER, Comm. Nos. 116, 122*a*, 124*a*.

tions again raised the idea that the distance of the molecules in a paramagnetic substance certainly has an influence upon the deviations from CURIE's law. Their investigation of oxygen of more than 100 times the normal density (Comm. N°. 134*d* April 1913) demonstrated more specially that the susceptibility for gaseous oxygen can be represented down to — 130° C. with CURIE's constant, which holds for the ordinary temperature, which indicated the possibility that this might still be the case at — 183° C. This gave fresh support to what they added at the end of their paper of Jan. 1913 (Comm. N°. 132*e*), showing the desirability of experiments upon the question, whether the bringing of the molecules (or atoms) of a paramagnetic substance to a greater distance from each other, influences in itself the deviations from CURIE's law, and pointing out the importance of the continuation of our experiments with liquid mixtures of oxygen and nitrogen. [1])

Before we could at last begin these experiments in 1913 the importance of them was increased by yet another circumstance. Besides the hypotheses considered in the above mentioned article, hypotheses of another kind arose [2]).

With the former hypotheses, we do not interfere with the law of equipartition, but assume either polymerisation, as in the above case, or a subsiduary potential energy, a "molecular" field, the magnitude of which is determined, not only by the field, but also by the amount of one-sidedness of the direction of the molecular magnetic axes (WEISS and FOËX, KAMERLINGH ONNES and OOSTERHUIS) [3]). In the new type (OOSTERHUIS, KEESOM) on the other hand a distribution of energy

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[1]) Recently, WEISS (C. R. Dec. 1913) in deducing the distance law for the molecular field in ferromagnetic substances (comp. § 4 this Comm.) points out the importance of investigations of the same material at different densities. See also G. FOËX, Arch. d. Sc. phys. et natur. Genève (4) XXXV. 1913.

[2]) As had been partly the case with the hypotheses of the first kind, so also those of the new kind were partly suggested by our former magnetic investigations.

[3]) The hypothesis, that the resultant magnetic moment of the molecule changes, can be introduced in two different ways. In the first place, by assuming polymerisation, as mentioned above. In the second place by supposing that the change takes place exclusively within the molecule itself. By continuous change of this sort of course every deviation from CURIE's law may be explained. In that case there can be no question of decision between the above mentioned types of theory. The supposition referred to seems less acceptable also for this reason that in the cases in which WEISS was led to assume a change in the molecular moment, this was always a discontinuous alteration (by changes in the number of magnetons) and one which took place in all the molecules at once, while for the rest the moment within a definite temperature zone did not undergo any change.

is supposed, which is determined according to the quantum-theory.

In the extreme form of this type no other suppositions are introduced than those of the quantum-theory. There is naturally room for transitional forms between this extreme form and the other type of hypothesis. These are got by assuming polymerisations or a molecular field besides the quantum-theory.

It is now of importance, not only for magnetism, but also for the law of molecular activity in general, to decide between these two different types of hypothesis, by experiment. The most important for this purpose are experiments in which the paramagnetic molecules are brought to different distances from each other. For if the above mentioned question should be answered in the negative and it should be proved that the susceptibility per molecule remained the same at whatever distance they are from each other, then all hypotheses of the first sort (mutual influences) would of course fall to the ground. The measurements which should demonstrate this would be an experimentum crucis.

The determination of the susceptibility of liquid mixtures of oxygen and nitrogen claims the first place in experiments upon the influence of the distance of the molecules upon the deviations from CURIE's law. The liquid (paramagnetic) oxygen exercises no chemical influence whatever upon the liquid (diamagnetic) nitrogen ; the two substances can be mixed in any proportions, so that the distance of the paramagnetic oxygen molecules can be increased at pleasure : the mixtures remain moreover liquid down to a very low temperature, which is of particular importance, if the theory of quanta is to be applied. Experiments with these mixtures promised therefore a more distinct and more immediate decision than those with crystals and solutions of chemical compounds in different degrees of dilution [1]). In the investigation now completed we have not been able to do more than make a first survey of the difficult territory.

We here offer our sincere thanks to Dr. OOSTERHUIS, who has contributed greatly to the success of our work, by very carefully measuring out the field that served for our experiments, and by repeating certain susceptibility determinations which were doubtful. His measurements enabled us to introduce important corrections in our results.

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[1]) With regard to these we may remark that the important investigations by CABRERA and MOLES (Arch. d. Genève (4) XXXV, May 1913) of solutions of iron salts are of a chemical nature and assume the validity of CURIE's law. Their object is therefore quite different from ours, in which the point is to investigate the influence of the distance of the molecules of a *chemical element* dissolved in another *element*, upon a function of the temperature.

§ 2. *Method.* The measurements were made by the attraction method, with a vertical cylinder of the substance to be investigated. One of the extremities of the cylinder is placed in the middle of the interferrum of an electromagnet. As in the apparatus previously constructed by us [1]) the cylinder was attached to a vertically running carrier, and the forces were measured by a zero-method; in this the modification introduced by OOSTERHUIS [2]) was made use of, viz. the current through the electro-magnet was regulated, and therefore the field adjusted, until there was equilibrium with marked weights.

While thus the magnetic part of the experiments is about the same as that of the previous ones, the arrangement of the actual experimental object demands a number of special apparatus and precautions. A homogeneous mixture must be prepared of known proportion, and in a proportion chosen at will, of two substances, which are gaseous at ordinary temperature, and which are condensed in the experimental tube.

In the first place a communication must be made through the closed outer cover of the cryomagnetic apparatus (see description loc. cit.) with the apparatus for mixing and measuring the gases. For this purpose, the glass tube *A* (see fig. 1), which forms the central part of the carrier, is bent round three times rectangularly at *B*; further it bears a horizontal tap *C*, and terminates in a horizontal ground joint *D*, in which fits the ground extremity of the tube *E*, which protrudes outside. This tube is enclosed in a thick but elastic india-rubber covering, and can be pulled back about 2 centimetres, from outside, and made fast in this new position; in this way the connection with the carrier can be made; or the latter can be left *quite free*, without the cover being opened. In the same way the tap *C* can be manipulated from the outside by means of a similar arrangement *F*.

The necessity of the mixture being homogeneous, entails vigorous stirring inside the experimental tube (the cylinder *R*, at the lower end of the carrier). Even when the mixture is homogeneous in the gaseous form, the oxygen which condenses more easily, will tend to collect at the bottom in the carrier; this difficulty is overcome by using a stirrer consisting of a very long thin glass capillary tube *G*, terminating in a small disk *H* (the actual stirrer), which carries a little piece of iron (*K*) at the top; the whole of which can be moved up and down through a distance equal to the height of the experimental tube. This movement is set in motion by the attraction

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[1]) See H. KAMERLINGH ONNES and ALB. PERRIER, Comm. No. 139*a*.

[2]) E. OOSTERHUIS, Comm. N⁰. 139*b*.

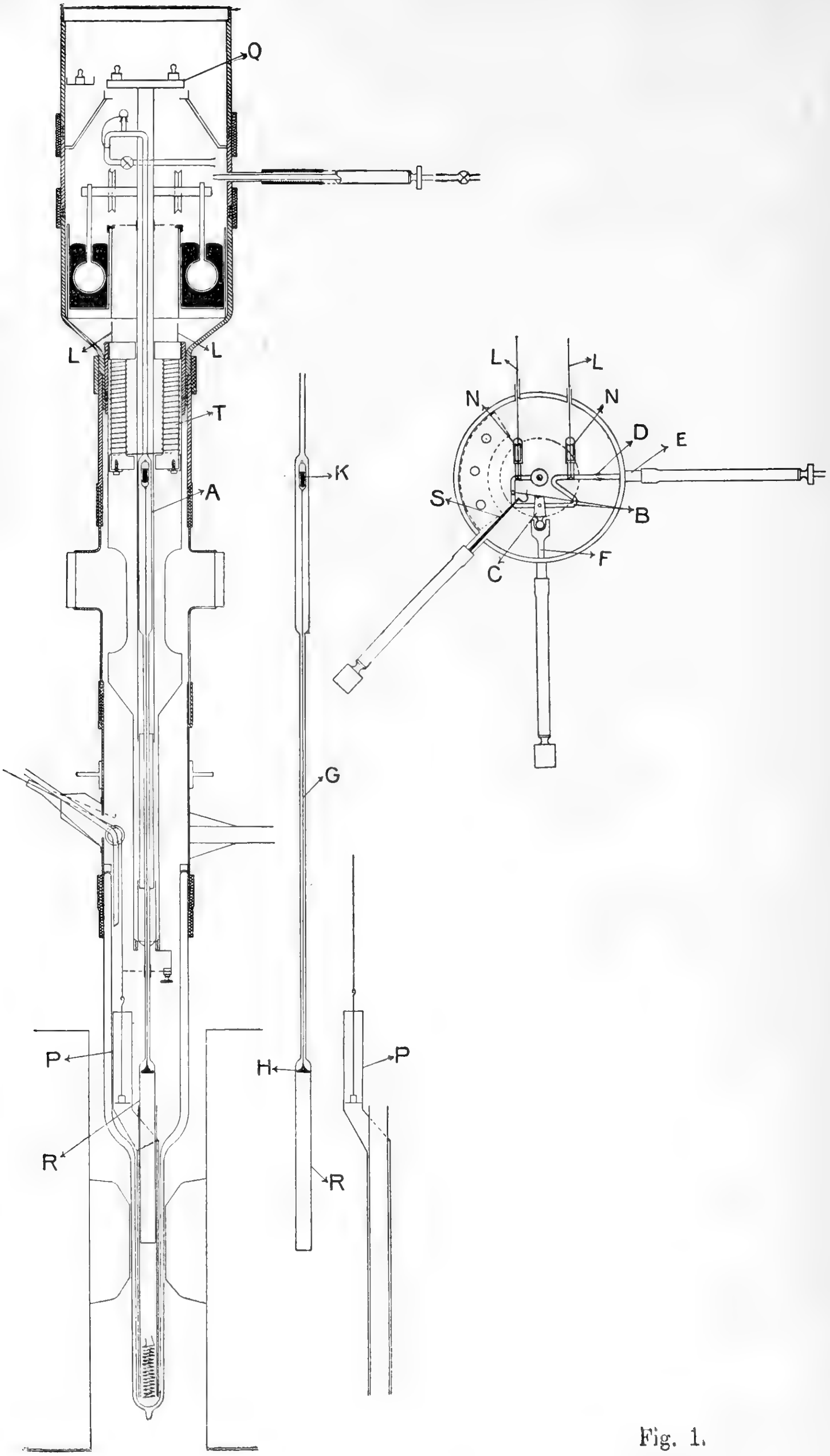

Fig. 1.

of an electromagnet I upon the piece of iron K; the electro-magnet is moved from outside the apparatus by means of two bronze strips L, which run over the pullies N and pass through the walls without friction, terminating in two elastic enclosures similar to F and E. These suspension-strips, which also serve as conductors for the electro-magnet, are moved by hand.

The carrier is provided at B with a small stopper serving as a safety valve, to guard against a casual excess of pressure in the carrier during the measurements, when the tap is closed, bursting the carrier.

The preparations for a series of measurements took place in the following order: when the enclosure is found to be air-tight, a sufficient weight is placed upon the plate Q to bring the carrier to its lowest position; the connection with the tube E can then be made, the tap C is then opened, and any gases that may be contained in the carrier, are pumped out. Then the cryogen bath (of pure liquid nitrogen) is made ready, and the temperature reduced to a few degrees below the boiling-point by reduction of the pressure. Finally the desired amount of pure oxygen, which has been previously measured in a volumenometer resembling a TÖPLER-pump, can be condensed in the carrier, and then by means of the same instrument, the quantity of pure nitrogen required to completely fill the experimental tube R. After this C is shut, D is disconnected, the gas supply tube is pulled back and the overweight taken away; the carrier is then free, and completely closed against the vapour of the bath. While the bath is being brought to atmospheric pressure, and to an even temperature, which is greatly promoted by the pump-stirrer P 1), which causes a vertical circulation in the whole bath, the electro-magnet which serves as stirrer for the mixture, is put in motion, until the magnetic attraction, which is measured from time to time, reaches a constant value.

The question of what the composition of the mixture is deserves particular attention. A *given weight* of oxygen is introduced into the tube, which spreads over a given volume, known by the calibration of the experimental tube. The weight of oxygen per cm^3., i. e. the concentration, is thus given by immediate experiment, which quantity is also the most important from the magnetic point of view, as the measurements in the first place give the susceptibility of the mixture, and the concentration enables us to deduce from it the specific magnetism which can be ascribed to the oxygen

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1) See H. KAMERLINGH ONNES, Comm. No. 123, § 2.

alone. To compensate the vacuum caused by the contraction of the mixture by each decrease of temperature, we have each time added *pure nitrogen* (stirring of course each time); our object was the investigation of the influence of the mean *distance* of the paramagnetic molecules upon the magnetisation, and the process described above apparently comes to the determination of the changes in the magnetisation with the temperature, for every mixture at *constant distance* of the oxygen molecules.

After the measurements the vapour products were collected, and analysed with pyrogallic acid. This analysis is a useful check, but cannot lay claim to great accuracy, as the comparison with the synthesis assumes the knowledge of the total quantity of condensed nitrogen (including the amount added during the measurements), which quantity is for various reasons somewhat uncertain. Moreover it is necessary that the vapour products should be very completely collected, as a considerable weight attaches to what is vaporised last, as being almost pure oxygen. On the other hand we may remark that the deduction of the concentration (see above) from the synthesis presumes only an accurate knowledge of the *weight of oxygen* and not that of the nitrogen, and therefore can claim a greater degree of accuracy.

The susceptibilities are expressed in absolute units by comparison with that of pure liquid oxygen, which are previously measured in absolute value by the method of rise ¹); this calibration comes simply to this, that a series of measurements are made under the same conditions as the former, but with pure oxygen instead of with the mixtures. Moreover, a calculation of the absolute values based upon the values of the field according to the measurements made by Dr. OOSTERHUIS in Leiden after the measurements, lead to results which agreed with the experiments previously obtained, well within the limits of experimental accuracy. Further the magnetic corrections were applied for the glass of the carrier and for the nitrogen of the bath as well as of the mixture ²).

§ 3. *Conclusions and experimental results.* The mean numerical data of the measurements are given in table I, where χ signifies the magnetisation of 1 gram of oxygen in each of the mixtures or in the pure oxygen; for the latter the values are calculated on the

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¹) KAMERLINGH ONNES and PERRIER, Comm. No. 116. Cf. note 1, p. 912.

²) These corrections must be made even in a purely relative measurement, as they are by no means proportional to the susceptibility of the experimental object taken as a whole.

basis of our measurements in 1910 (Comm. N°. 116); ϱ is in each case the weight of oxygen per cm³. (concentration), λ the approximate ratio between this weight and the corresponding one in the pure liquid; λ indicates to some extent the dilution (only approximately, because with the method followed λ changes with the temperature)[1].

TABLE I.

Magnetisation-coefficients for oxygen. (77.°4 K—64.°2 K)

		ϱ		(p = atm. pressure)		(p = 300 mm.)		(p = 100 mm.)	
				t	$\chi . 10^6$	t	$\chi . 10^6$	t	$\chi . 10^6$
liquid oxygen pure		1.204		$-195^\circ.65$	259.6				
		1.235				$-202^\circ.2_3$	271.4		
		1.267						$-208^\circ.8_4$	284.9
Mixtures	I	0.745_8	$\frac{3}{5}$	$-195^\circ.65$	294.5	$-202^\circ.2_3$	314.5	-208.8_4	336.5
	II	0.401_0	$\frac{1}{3}$	.79	336.7	"	359.6	"	390.6
	III	0.230_4	$\frac{2}{11}$	.60	363.8	"	393.0	"	[423.5]
	IV	0.138_0	$\frac{1}{9}$	.65	383.6	$-202^\circ.2_3$	420.4	"	459.8
	V	0.080_1	$\frac{1}{15}$	$-195^\circ.80$	395.8	—	—	-208.8_4	472.0
extrapolated by $\chi = \frac{0.03097}{T}$ (WEISS and PICCARD at 20° C.)				$-195^\circ.65$	400.0	$-202^\circ.2_3$	437.2	$-208^\circ.8_4$	482.2

Table I shows at once this qualitative result: *The specific magnetisation coefficient of oxygen becomes considerably greater, in pro-*

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[1] The various numerical data upon which the results are based are not all of the same degree of accuracy: the temperatures, measured by means of the pressure under which the liquid boils, the same pressures being chosen for the different mixtures, may be compared in the one and the other mixture to 0.1°, the absolute values, on the other hand, have the same degree of accuracy as the vapour pressure curves.

The directly found (volume) susceptibilities of the mixtures, which are not included in the table, may be compared with one another to about 0.3% on an average. As regards the *specific magnetisation coefficients*, if these may be compared *for the same mixture* at different temperatures with the same accuracy as the susceptibility, their uncertainty in *absolute value* is specially determined by that of the concentration; we estimate it on an average at 1.5%, higher for the large concentrations, lower for the smaller ones.

portion as the concentration diminishes, i. e. the additive rule is by no means followed in mixtures of oxygen and nitrogen. From a somewhat more careful inspection, and the comparison with the last row of the table, it appears further that *with increasing dilution the magnetisation coefficient approaches to the values which satisfy the inverse proportionality with the absolute temperature,* starting from the number lately obtained by WEISS and PICCARD for gaseous oxygen (see also Fig. 3).

Without anticipating in any way the theoretical interpretation of these results, which will be treated in the next paragraph, we can phenomenologically express them as follows:

The deviations from CURIE-LANGEVIN's *law, shown by pure oxygen at low temperature, are not an immediate consequence of the change of temperature, but are caused by the increase of the density or by the distance between the molecules becoming smaller.*

Finally, let us examine more closely the *thermal change* for *each concentration,* by plotting $^1/_\chi$ as a function of T (Fig. 2). We see at once that the points obtained lie upon *parallel straight lines*; the

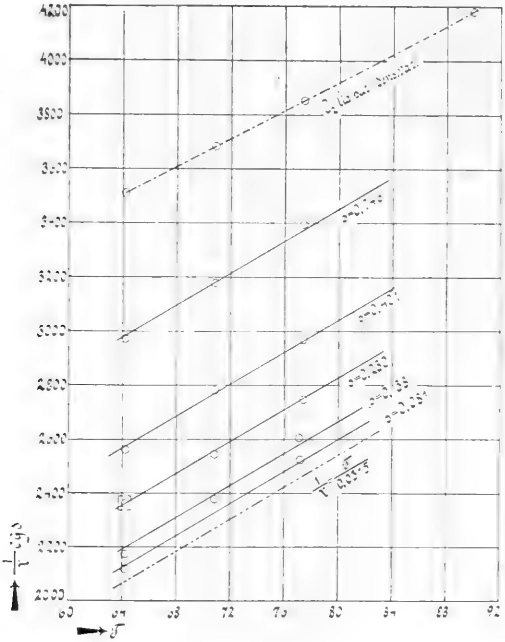

Fig. 2.

change with the temperature can therefore be represented [1]) within the limits of accuracy of the observations, by a relation of the form

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[1]) As was found by KAMERLINGH ONNES and OOSTERHUIS for liquid oxygen; Comm. N⁰. 132*e*.

$$\chi(T+\Delta) = const.,$$

in which only the parameter Δ changes from one concentration to the other. Table II shows this:

TABLE II.

Mixture	Δ	$\chi(T+\Delta)$		
		$T=77.4_4$	$T=70.8_6$	$T=64.2_5$
I	29.5	0.0315	0.0316	0.0315
II	16.3	316	313	315
III	9.5	316	316	[312_5]
IV	4.5	314	316	316
V	2.2	316	—	314
Mean 0.0315_2				

Therefore: the *change in density of the oxygen only alters the specific magnetisation, without changing the* Curie-*constant.*

The pure liquid oxygen seems to form an exception: the straight line $^1/_\chi = f(T)$ for this differs considerably in direction from that for the mixtures. We would call attention to the fact, however, that each mixture was examined at constant concentration (see § 2); while this was not the case with pure oxygen, which shrinks considerably on cooling (10 $^0/_0$ about between — 183° and — 210°); if we calculate for any temperature (say —195°) the specific magnetisation that pure oxygen would have at that temperature and at the densities corresponding to the other temperatures, using the Curie-constant which is common to the mixtures at constant concentration, the values obtained thus (see Fig. 3 the points indicated by black disks) fall in a natural way upon the general curve, which gives the specific magnetisation as a function of the concentration at the temperature under consideration; the data obtained from these measurements form therefore strong arguments in favour of the conclusion that in the investigation of *pure liquid oxygen at constant density a curve for the change of the magnetisation would appear, which only differed from that for the mixtures by a new translation.* This causes the anomaly to disappear. The strict experimental proof of this conclusion can only be obtained by a great number of experiments with a very concentrated liquid, or by means of a direct experiment, in which we begin

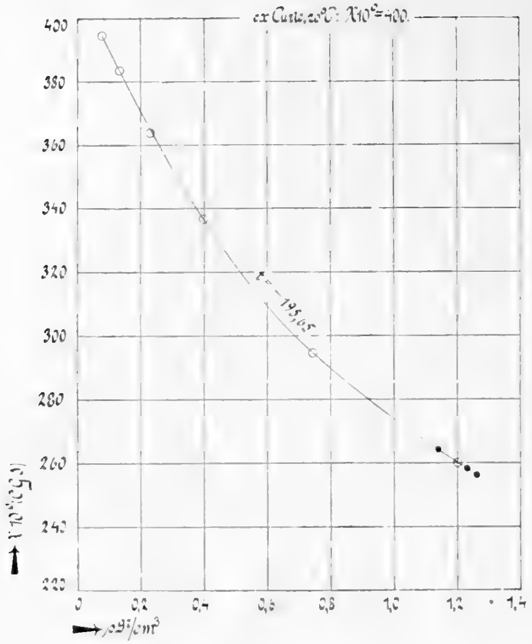

Fig. 3.

with pure oxygen and for each decrease of temperature add the necessary quantity of nitrogen [1]).

§ 4. *Theoretical conclusions.* We must call attention to the fact that every theoretical interpretation of our results must account for two different facts: in the first place for the change of the magnetisation with the density, and in the second place the parallelism of the lines $\frac{1}{\chi} = f(T)$.

It is plain that LANGEVIN'*s theory, only supplemented by the hypothesis of the negative molecular fields, is sufficient to give the explanation.* In fact if N represents the coefficient of the molecular field, it leads to the law

$$\frac{1}{\chi} = \frac{T}{C} + N\varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$\chi (T + \Delta) = C, \text{ where } \Delta = CN\varrho,$$

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[1] Experiments make it probable, that for gaseous oxygen χ even at -183° C. does not deviate or at least (see the conclusion of § 4) deviates only very little from CURIE's law. In the application of the ascension method χ may therefore not be supposed to be equal for the liquid and for the vapour, as was done in formula (2) of Comm. No. 116, but a correction must be applied, which, however, in our case remains within the limits of experimental error.

which agrees with the law following from Table II, if we assume that Δ or $N\rho$ *decreases with the density.*

This being established, the experiments further permit, and this gives them an additional significance, to account for *the way in which the molecular field changes with the density or with the distance of the molecules.*

We remark in the first place, that the accurate calculation of the molecular fields rests upon the knowledge of the *deviations from* CURIE'*s law,* and not upon that of the susceptibilities themselves [formula (1)]. It would therefore be necessary to know the specific magnetisations in absolute value down to at least 0.1 °/₀ in order to be able to deduce the fields from them with sufficient certainty; this is especially the case for the great dilutions where the deviations are extremely small. A determination of this degree of accuracy demands in itself a long and difficult special investigation with perfected apparatus.

The solution, if not completely found, may yet be brought within narrow limits. The first question that then arises is, whether the field is equal to a particular power of the distance of the molecules i. e. of the density. If we suppose $N = a\rho^n$, then the molecular field is $a\rho^{n+1}$. At constant temperature $^1/_\chi = f(\rho)$ is then a parabola of the degree $n+1$, with the axis vertical and the top on the axis of ordinates. For $n = 0$, $^1/_\chi$ is represented by a straight line.

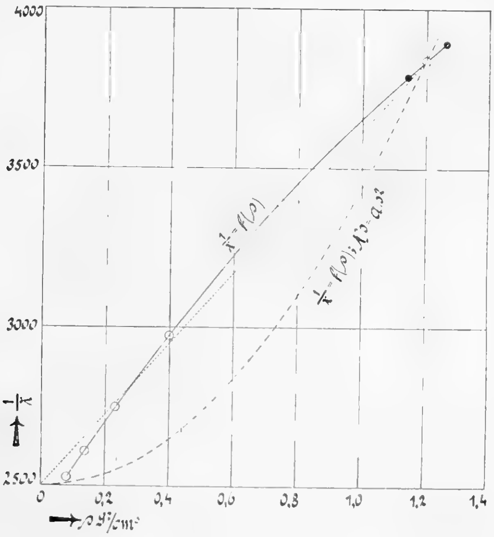

Fig. 4.

In Fig. 4, the curve which our experimental data give for the temperature 77°.45 K. is shown; it deviates from the straight line, but the deviations are not much greater than the errors of observation, except for the most diluted mixture. Moreover the slight curvature is *in the opposite sense to all the parabolae for which* $n > 0$. The observations at concentrations smaller than 0.1 indicate that the molecular field then begins to change more quickly, but they do not justify the assertion that this is actually the case. It is therefore not probable that the results can be represented by means of a positive n (except for very great dilutions, for which we have not a single indication); in order to elucidate this point we have also constructed the curve $^1/_\chi = f(\varrho)$, which with the same extremities corresponds to $n = 1$, i. e. to the law that the molecular field would be proportional to the square of the density or to the inverse sixth power of the mean distance of the molecules; it is obvious that this bears no resemblance to the experimental curve.

We assume therefore *that the molecular field of oxygen changes about proportionally to the density*[1]).

This law, in the case of the appearance of a negative field (assuming that this exists) for oxygen, differs totally from that at which WEISS arrived, in the case of the positive molecular field with alloys of ferromagnetic metals, for the dependence of N upon the density, and from which he inferred an influence according to the inverse sixth power of the distance, which for that reason we have just referred to. (From our law, in the same way, an influence according to the inverse third power of the distance would follow).

At present, we need not see any contradiction between these two results, as the conditions for which the two laws of distance hold good, are quite different. This applies both to the nature of the substances and to the state of aggregation in which they were examined. Moreover it must be particularly borne in mind that the sign for the molecular field is different in both cases. The part of the curves referring to the change of N with the concentration, which WEISS makes use of in his theory, lies entirely in positive fields, the transition to negative fields is curved. We are in complete ignorance as to the origin of the mysterious influences which cause the phenomena ascribed to the molecular field. There is no ground therefore to expect that the two fields are subject to the same law. Should it be confirmed that the two kinds of molecular field depend upon the distance of the molecules according to different laws, we

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[1]) Cf. the next paper by KAMERLINGH ONNES and OOSTERHUIS, in which the idea of the dependence of $\triangle$ on the concentration is extended to the "atomic concentration" of the paramagnetic component in crystallized compounds, in the first place in those containing water of crystallization.

might even see in this a proof that in the two cases influences are at work which are the effect of different causes [1]).

If we continue the idea that the deviations from Curie's law are to be attributed to a negative field, we come with the value 0,03152 which we deduce for Curie's constant, to 14.11 magnetons per molecule of 2 rigidly connected atoms, while Weiss and Piccard, from their determination of the constant for gaseous oxygen arrive at exactly 14. An error of 0.2 degrees in the lowest temperature at which we made observations would explain this difference. So there is no reason to take this observation as at variance with the law of magnetons. [At the end of § 4 we have drawn attention to a circumstance that would possibly explain the difference. (Added in the translation)].

Although the hypothesis of the negative molecular field is sufficient to describe the phenomena, it is not devoid of interest to consider in how far the other hypotheses can be reconciled to the observations.

As regards the polymerisation-hypothesis, it is not probable that the association decreases as rapidly with the density at constant temperature as would have to be the case if the experiments were to be explained by it, nor that the result of a given form of the hypothesis, which might give this change, would lead to the set of parallel straight lines in fig. 2.

Oosterhuis's hypothesis, that the energy of rotation should take the form of

$$U_r = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{h\nu}{2}$$

must be supplemented by a further hypothesis. It is in the line of the deduction to accept that the moment of inertia of the molecule changes considerably by dilution, and increases to very great values. Even in accepting this hypothesis it appears from calculations by Dr. Oosterhuis that the deviations of the curves calculated from the set of the parallel straight lines in fig. 2 are too large to be explained by experimental errors [2]).

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[1]) The function $\rho^{4/3}$, which was given in a preliminary note (Soc. Suisse de physique, Frauenfeld 1913) was based upon data which later appeared to have been insufficient in number, and before some subsequently calculated corrections had been applied. The function may be correct for a range of weak concentrations.

[2]) In these calculations Oosterhuis started from the values of Δ which were deduced immediately from the experiments according to Table II, which in particular gives the most probable slope of the straight lines accepted to be parallel.

Finally we may remark that the supposition

$$^1/_\chi = f(T) + N\varrho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

combines the various hypotheses which we have explained above (except that of polymerisation), and agrees with our experiments if $f(T)$ is independent of the density, and N of the temperature [1]). It accounts for all phenomena which are expressed by a parallel displacement whatever value is ascribed to $f(T)$, if only it remains independent of the density.

[One can imagine that $f(T)$ is in reality of such a form that in the temperature-range of our experiments it gives for χ of the oxygen in the liquid mixtures of oxygen and nitrogen a value which, while being small for the large densities of oxygen, increases in passing to more and more high dilutions, and approaches in the limit to a value *greater* than that which with CURIE's law is obtained from WEISS and PICCARD's experiments. If further experiments which may be undertaken with a view to throwing light upon this point should give a positive result, one could explain without relying upon experimental error the slope of our lines for $^1/_\chi$ being a little small (given by $C = 0{,}0315$, see fig. 2). It would then be of interest to compare that result with what the investigation by KAMERLINGH ONNES and OOSTERHUIS on the susceptibility of gaseous oxygen at low temperatures will teach when extended to lower temperatures. It is not entirely excluded that the nitrogen plays a different part from a vacuum. Added in the translation.] (Cf. note 1 p. 915. Added in going to press).

Since then Dr. KEESOM has communicated to us that by calculating the values of Δ in giving to $f(T)$ [see formula (3)] either OOSTERHUIS's form, or the form which KEESOM has developed in Suppl. N°. 32*a*, whereby the values of Δ are a little changed, one obtains a satisfactory representation. The values of Δ are then in agreement with the function $\varrho^{2/3}$ for large values of ϱ, which he arrives at (see a paper of his to be published shortly). In his calculations KEESOM accepted the number of magnetons of WEISS and PICCARD. His theory explains also that the curve $^1/_\chi = f(\ )$ of fig. 4 does not pass through the origin. [Note added in going to press.]

[1]) $f(T)$ represents the energy of rotation as a function of the temperature. (3) is only applicable to the range where the magnetisation is strictly parallel to the field. Formula (3) includes inter alia the vanishing of the CURIE point in ferromagnetic substances caused by zero energy deduced by KEESOM (Leid. Com. Suppl. N°. 32 *a* and *b* (1913).

[Regarding the influence of the density on $f(T)$ in KEESOM's theory see his next paper, cf. also note 2 p. 6 of Suppl. N°. 32*a*. Added in going to press.]

Physics. — "*Magnetic researches.* XIV. *On paramagnetism at low temperatures*". (Continuation of VII). By H. KAMERLINGH ONNES and E. OOSTERHUIS. Communication N°. 139*e* from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

§ 15. *Ferrous sulphate.* (Continuation of III § 2). The measurements of the susceptibility of paramagnetic substances at low temperatures were continued according to the method previously described.

Crystallized ferrous sulphate, which had been already investigated by KAMERLINGH ONNES and PERRIER (Comm. N°. 122*a*), was once more very carefully prepared, by precipitating it out of its aqueous solution with alcohol. The values of the susceptibility found do not entirely correspond to the previous ones, but the dependence on the temperature is precisely the same, as is shown by the following table, when compared with table II of Comm. N°. 122*a*,

TABLE XII.

Crystallized ferrous sulphate $FeSO_4 . 7H_2O$ precipitated with alcohol.

$T.$	$\chi . 10^6$	$\chi . T. 10^6$	Bath
292.°3 K.	42.4	12390	in air
77.3	160	12370	liquid nitrogen
64.6	191	12340	
20.2	571	11590	liquid hydrogen
14.7	756	11110	

§ 16. *Palladium.* Pure palladium (from HERAEUS) gave the following figures: (see p. 918)

Palladium, it will be seen, deviates markedly from CURIE's law. CURIE found just for this substance the law $\chi . T =$ const. fairly well confirmed. HONDA [1]) (above ordinary temperature) and OWEN [2]) (below ordinary temperature down to 100° K.) found deviations from CURIE's law which agree very well with our results. The line $\frac{1}{\chi} = f(T)$

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[1]) K. HONDA. Ann. d. Phys. 32, p. 1027, 1910.

[2]) M. OWEN. Ann. d. Phys. 37, p. 657, 1912.

TABLE XIII.

Palladium.		
T	$\chi \cdot 10^6$	Bath
291° K.	5.3	in air
250	5.8	liquid methyl chloride
212	6.0	
170	6.9	liquid ethylene
77.3	8.1	liquid nitrogen
70.2	8.2	
64.6	8.3	
20.3	9.9	liquid hydrogen
17.9	10.2	
14.7	10.9	

shows some irregularities, which are greater than we should have expected considering the degree of accuracy of the experiments.

§ 17. *Ferric ammoniumsulphate (iron alum).*

This substance will be seen to follow CURIE's law throughout the whole range of temperature that was examined. This, according to the theory developed by OOSTERHUIS in Suppl. No. 31, would be owing to the great moment of inertia which a molecule of this substance undoubtedly possesses.

It may also be explained by the theory which FOËX gives following WEISS (C. R. T. 157, p. 1145. 1913). In fact iron alum is a substance crystallizing in the regular system and according to FOËX, for such substances the line $\frac{1}{\chi} = f(T)$ will be a straight line at all temperatures.

This property of ferric alum may also be regarded from another point of view if we consider the latest results by KAMERLINGH ONNES and PERRIER (Comm. N°. 139*d*). In § 3 we pointed out that interposition of water molecules between the molecules of ferrous sulphate, as occurs when this salt crystallizes with water of crystallisation, causes the deviation from CURIE's law to disappear, and thus diminishes Δ.

TABLE XIV.

Ferric ammoniumsulfate $Fe_2(SO_4)_3 . (NH_4)_2SO_4 + 24H_2O$.			
T.	$\chi . 10^3$	$\chi . T . 10^3$	Bath
290.°0 K.	30.4	8820	in air
169. 6	51.8	8790	liquid ethylene
77. 3	114.7	8870	liquid nitrogen
64. 6	137.0	8850	
20. 4	432	8810	liquid hydrogen
17. 9	492	8810	
14. 7	598	8790	

We found the same in § 10 for manganese sulphate, and in § 11 we came to the conclusion that the decrease of Δ might be the consequence of an increase in the distance of the paramagnetic constituents of the salt. Finally, we drew attention to the fact that the transition of oxygen from the gaseous to the liquid form might be accompanied by a change in Δ. PERRIER and KAMERLINGH ONNES have now demonstrated that Δ decreases with the dilution of oxygen with nitrogen, and that the change of Δ with the density, which must be assumed to find for liquid oxygen at all temperatures [with the help of the $\Delta_{\rho\, liq\, T}$ corresponding to the liquid density $\rho_{liq\, T}$] from

$$\chi (T + \Delta_{\rho\, liq\, T}) = C$$

the same number of magnetons as in the gas at ordinary temperature, agrees well with the change of Δ with the distance of the molecules, which is found from the dilution of oxygen with nitrogen. By this it has become evident that if Δ is the consequence of the existence of a molecular field, this field decreases when the molecules are brought to a greater distance from each other, and soon, at molecular concentrations of about $\frac{1}{200}$, is no longer perceptible.

In ferric alum, the distance of the *Fe*-atoms is of the same order as that at which the molecular field of the oxygen molecules in the solution of oxygen and nitrogen disappeared in KAMERLINGH ONNES and PERRIER's experiments. That this substance conforms to CURIE's law as far down as the freezing-point of hydrogen, may therefore be due to the atoms of iron, at the *atomic concentration* in this substance, being at a distance which permits them to behave like those of a normal paramagnetic substance. Should this hypothesis be correct, it would be of importance to take notice of the atomic concentration, in studying paramagnetic substances. To determine the number of magnetons in a paramagnetic atom, we should therefore have to take (complex) compounds, which fulfil this condition of being sufficiently "diluted". This condition is fulfilled by many of the materials which have been used for the calculations about magnetons [1]).

If we arrange the substances according to the value of their atomic concentration, we see that in general the deviations from CURIE's law at low temperatures seem to appear sooner in substances with a high concentration. OOSTERHUIS's calculations (Comm. Suppl. N°. 31) give particulars of the amount of the deviation in different substances. It will therefore be desirable, if we want to determine the number of magnetons in an atom at low temperature, to go down to very small concentrations. This is no difficulty for the measurement, for, although the specific susceptibility at small concentration is small, it increases considerably according to CURIE's law for a given concentration with the transition to low temperatures. We should come upon chemical ground if we were to discuss what compounds would be suitable for this purpose. Double salts and complex compounds seem to be particularly suitable, provided we are able to apply the correction for diamagnetism.

It is very likely that with high atomic concentrations Δ may rise to very high values. Something of this sort might be the case with platinum (see § 12) and with the ferromagnetic substances the investigation of which first led WEISS and FOËX to the introduction of a negative magnetic field.

For crystals, a *"linear concentration"* may have to be introduced. The value of Δ for different directions would have to be brought into connection with this.

In the further study of the deviation from CURIE's law, use will have to be made of the results of WERNER's investigation of the constitution of complex compounds on the one hand, and on the other hand of the data which experiments upon the diffraction of RÖNTGEN rays, such as BRAGG in particular has made, may yield. What these can teach concerning the arrangement of the atoms and the structure of the atomic lattice, is of great importance from the above point of view. (*To be continued*).

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[1]) In ferric alum is realised a case of solution of a paramagnetic in a practically neutral substance, of the same kind as that which WEISS considered by extrapolation in his discussion of the ferro-magnetic alloys when he was searching for the law of distance for the molecular field.

Geology. — *"At what time the Indian Archipelago is separated from the Tethys"*. By Prof. K. MARTIN.

(Communicated in the meeting of January 31, 1914).

(This communication will not be published in these Proceedings).

(March 26, 1914).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Saturday March 28, 1914.

VOL XVI.

Vice-President: Prof. D. J. KORTEWEG.

Secretary: Prof. P. ZEEMAN.

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CONTENTS.

Physics. — *"A new relation between the critical quantities, and on the unity of all substances in their thermic behaviour."* (Continuation.) By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of February 28, 1914).

8. *The shape of the function* $b=f(v)$. After we have thus derived some relations in the preceding paper[1]), by means of which all the critical quantities are expressed in the one quantity γ, the reduced coefficient of direction of the so-called "straight diameter", we shall examine what forms of $b=f(v)$ satisfy the relations found.

These relations, from which the table on p. 829 loc.cit. has been calculated, are the following. [Cf. also the formulae (14) and (21) loc.cit. p. 818].

$$\left.\begin{array}{l} z=\frac{b_k}{v_0}=2\gamma \quad ; \quad r=\frac{v_k}{b_k}=\frac{1+\gamma}{\gamma} \quad ; \quad s'=\frac{v_k}{v_0}=2\,(1+\gamma) \\ s=\frac{RT_k}{p_kv_k}=\frac{8\gamma}{1+\gamma} \quad ; \quad \frac{s'}{s}=\frac{(1+\gamma)^2}{4\gamma} \quad ; \quad \lambda=\frac{27\gamma^2}{(1+\gamma)^2(8\gamma-1)} \end{array}\right\} . \quad (22)$$

In this λ is the factor in

$$RT_k=\frac{8}{27}\lambda_1\frac{a}{b_k} \quad ; \quad p_k=\frac{1}{27}\lambda_2\frac{a}{b_k^2},$$

in which $\lambda_1=\lambda_2=\lambda$ is put. The found values of λ_1 and λ_2 appeared, namely, not to differ, and λ is always in the neighbourhood of unity. Though γ varies from 0,9 for "normal" substances to 0,5 for "ideal" substances, λ ranges only between the values 0,98 and 1.

We further found:

$$\left.\begin{array}{l} f'=\frac{f}{1+\varphi}=8\gamma \quad ; \quad b'_k=\frac{(2\gamma-1)^2}{4\gamma(\gamma+1)} \quad ; \quad 1-b'_k=\frac{8\gamma-1}{4\gamma(\gamma+1)} \\ -\beta''_k=-\frac{v_kb''_k}{1-b'_k}=\frac{f'-4}{f'}=\frac{2\gamma-1}{2\gamma} \end{array}\right\} . \quad (23)$$

In this $\varphi=\frac{r}{r-1}\beta'_t$, in which $\beta'_t=\frac{T_k}{v_k}\left(\frac{\partial b}{\partial T}\right)_k$. We saw that β'_t is generally exceedingly small.

We may still remark that the relations for b'_k and b''_k may also be written thus:

$$b'_k=\frac{(b_k-v_0)^2}{b_k\,v_k} \quad ; \quad -b''_k=\frac{b_k-v_0}{b_k\,v_k}(1-b'_k)\,, \quad . \quad . \quad . \quad (24)$$

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[1]) These Proc. p. 808.

which enables us to find out something about the course of the function $b=f(v)$. For the sake of accuracy the original v_0 is everywhere written in the above formulae, and not the b_0 put equal to it. The quantity v_0 is namely the liquid volume at $T=0$ extrapolated from the equation of the straight diameter. From $^1/_2\,(d_1+d_2)-1=\gamma\,(1-m)$ follows namely, when $d_2=0$ and $m=0$, that the reduced limit of density $(d_1)_0$, i.e. $v_k:v_0$, becomes equal to $s'=2\,(1+\gamma)$. It is this v_0 which occurs in the above relations.

In virtue of the fact that when the limiting volume of b corresponding to this limiting volume v_0, i.e. b_0, is assumed different from v_0, very intricate, if not impossible results are obtained for $b=f(v)$ — whereas the assumption $b_0=v_0$ leads to comparatively simple results, I have been led to identify b_0 with v_0. So we assume that at the limiting value of v for $T=0$ (calculated from the formula of the straight diameter) also $b=v$, and so also $p=\infty$. Hence what we call v_0 and b_0 in what follows is the same as VAN DER WAALS understands by v_{lim} and b_{lim} [1]) — with this difference, however, that $\left(\frac{db}{dv}\right)_0$ is *not* $=1$, but always much smaller than 1, and will even appear to be $=0$ (at $\gamma={}^1/_2$). That the latter is really the case, follows also from this, that in the limiting case $\gamma={}^1/_2$ (ideal substances) — where therefore $b_g=b_0$, and the course of the function $b=f(v)$ is represented by a *straight line* parallel to the v-axis — necessarily b'_0 must be $=0$.

Let us now proceed to determine the shape of the function $b=f(v)$. According to what was observed in § 1 of the foregoing paper, we consider the variation of b with the volume entirely as an *apparent change*, and that chiefly on the ground of the joint action of two influences, the diminution of the factor 4 in $b_g=4m$ ($m=$ nucleus volume of the molecules) to about $2m$ at b_0 — at least at the ordinary temperatures; and the simultaneously acting influence of temporary molecule aggregations (quasi association). These two influences will make the quantity b in $v-b$ diminish from $4m$ to about $2m$.

But at very low temperatures, at which b_g will approach more and more to b_0 (see § 7 loc. cit.) till $b_g=b_0$ at $T=0$, this variability disappears — and the question rises how this is possible. Does $b_0=2m$ then rise to $b_g=4m$, or does $b_g=4m$ descend to

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[1]) These Proc. XV p. 1132 at the top, 1138 and p. 1142 at the top, where everywhere $v_{lim}=b_{lim}$ is assumed. On p 1138 also $v_{lim}=v_0$ (from the straight diameter) is put. Our v_0 and b_0 are therefore exactly the same quantities as VAN DER WAALS' v_{lim} and b_{lim}.

$b_0 = 2m$. The former is in contradiction with the experimental result that b_g, and so also b *decreases* with decrease of temperature; the latter seems in opposition to the theoretical result that for infinitely large volume b_g must always be $= 4m$, and cannot possibly therefore assume the value $2m$, however low the temperature may be.

Yet the latter is the only possible supposition. We shall return to this at the close of this paper, and we shall then propose a supposition which may be alleged as an explication of this apparently so singular behaviour.

9. Let us first consider the forms which present themselves most readily, but cannot satisfy the equations (24), in connection with the convergency to b_0 and v_0.

When we put generally:

$$b = b_g - \alpha f\left(\frac{v}{\beta}\right), \quad \ldots \ldots \ldots \quad (a)$$

in which $f(v)$ is such that this function becomes $= 0$ for $v = \infty$, and increases with decreasing v, then

$$b_k = b_g - \alpha f\left(\frac{v_k}{\beta}\right),$$

hence also

$$b = b_g - (b_g - b_k)\frac{f(v)}{f(v_k)}, \quad \ldots \ldots \ldots \quad (b)$$

when we briefly write $f(v)$ for $f\left(\frac{v}{\beta}\right)$.

From this follows:

$$b' = -\frac{b_g - b_k}{\beta}\frac{f'(v)}{f(v_k)} \quad ; \quad b'' = -\frac{b_g - b_k}{\beta^2}\frac{f''(v)}{f(v_k)},$$

hence

$$b'_k = \frac{b_g - b_k}{\beta}\frac{-f'(v_k)}{f(v_k)} \quad ; \quad -b''_k = \frac{b_g - b_k}{\beta^2}\frac{f''(v_k)}{f(v_k)},$$

therefore

$$\frac{-b''_k}{b'_k} = \frac{1}{\beta}\frac{f''(v_k)}{-f'(v_k)}.$$

But as according to (24) also

$$\frac{-b''_k}{b'_k} = \frac{1 - b'_k}{b_k - b_0}$$

we have necessarily:

$$\beta = \frac{b_k - b_0}{1 - b'_k}\frac{f''(v_k)}{-f'(v_k)} \quad \ldots \ldots \ldots \quad (c)$$

In consequence of this we have:

$$b'_k = \frac{b_g - b_k}{b_k - b_0}(1 - b'_k)\frac{(-f'(v_k))^2 : f''(v_k)}{f(v_k)},$$

from which follows for the relation $(b_g - b_k) : (b_k - b_0)$:

$$\frac{b_g - b_k}{b_k - b_0} = \frac{b'_k}{1 - b'_k}\,\frac{f(v_k)}{(-f'(v_k))^2 : f''(v_k)} \quad . \quad . \quad . \quad . \quad . \quad (d)$$

The equation (b), written in the form:

$$b - b_k = (b_g - b_k)\left(1 - \frac{f(v)}{f(v_k)}\right),$$

then becomes:

$$b - b_k = (b_k - b_0)\frac{b'_k}{1 - b'_k}\,\frac{f(v_k) - f(v)}{(-f'(v_k))^2 : f''(v_k)}, \quad . \quad . \quad . \quad . \quad (e)$$

in which b'_k in given by (24).

First Example.

$$f(v) = e^{-v/\beta}.$$

Then $f'(v) = \partial f(v : \beta) : \partial(v : \beta) = -e^{-v/\beta}$, and $f''(v) = e^{-v/\beta}$, so that we obtain:

$$b - b_k = (b_k - b_0)\frac{b'_k}{1 - b'_k}\,\frac{e^{-v_k/\beta} - e^{-v/\beta}}{e^{-v_k/\beta}},$$

as $(-f'(v_k))^2 : f''(v_k) = e^{-v_k/\beta}$

Hence we get:

$$b - b_k = (b_k - b_0)\frac{b'_k}{1 - b'_k}\left[1 - e^{\frac{v_k - v}{b_k - b_0}(1 - b'_k)}\right], \quad . \quad . \quad (25)$$

as β according to $(c) = (b_k - b_0) : (1 - b'_k)$.

But the equation (25) — which in the neighbourhood of the critical point of course perfectly accurately satisfies the conditions: 1) that at $v = \infty$ the value of b becomes properly b_g in connection with (d), and 2) that the equation at v_k for b'_k and b''_k gives the values determined by (24) — is quite deficient in the neighbourhood of v_0. It has, namely, also to satisfy there for *small* values of $b_k - b_0$, when γ is near $^1/_2$ (ideal substances). Now in this case with $b'_k = (b_k - b_0)^2 : b_k v_k$ (see (24)), and in regard of the circumstance that in consequence of b'_k becoming $= 0$, unity may be written for $1 - b'_k$, for $v = v_0$, $b = b_0$ we get:

$$\frac{b_k - b_0}{b_k - b_0} = \frac{(b_k - b_0)^2}{b_k v_k} e^{\frac{v_k - v_0}{b_k - b_0}},$$

in which within [ ] 1 has been omitted by the side of the infinitely large value of the exponential quantity. But now the first member of this equation $=1$, the second member becoming $=0\times e^{\infty}$, hence approaching ∞. Not until v_k-v_0 should be of the order b_k-b_0, by which the exponential quantity could be made of the order $b_k v_k:(b_k-b_0)^2$, could the above equation be satisfied. But then v_0 would get into the neighbourhood of v_k, when b_k-b_0 approaches to 0, i.e. when γ approaches to $^1/_2$, and this is impossible.

It is easy to see from the graphical representation that the indicated $f(v)$ intersects the v-axis already soon after v_k, in consequence of which b passes to negative values, so that there can be no question of a convergency to the point v_0, b_0.

And it is easy to see that this cannot be changed by changes in the form of the chosen exponential function. Nor can KAMERLINGH ONNES' function satisfy. For this function, viz.

$$b=b_g-(b_g-b_0)e^{-\alpha(v-v_0)}\ ,$$

leading after substitution of v_k and b_k, through which v_0 and b_0 are eliminated, to

$$b=b_g-(b_g-b_k)e^{-\alpha(v-v_k)},$$

is identical with (b), when $e^{-v/\beta}$ is substituted for $f(v)$, (α satisfy is then $={}^1/_\beta$),. For it would inevitably lead to the rejected equation (25).

And if this and suchlike functions are made to satisfy at v_0, b_0 — they will necessarily *not* satisfy at v_k, b_k, i.e. the values b'_k and b''_k will then entirely differ from the theoretical values indicated by (24).

Second example.

$$f(v)=\left(\frac{v}{\beta}\right)^{-\theta}$$

As β will disappear here, an exponent θ must still be added to satisfy the conditions (24), which exponent can then again be determined from (c), b_g being given by (d).

We now find:

$$-f'(v)=\theta\left(\frac{v}{\beta}\right)^{-(\theta+1)}\quad;\quad f''(v)=\theta\,(\theta+1)\left(\frac{v}{\beta}\right)^{-(\theta+2)},$$

and hence for $(-f'(v_k))^2:f''(v_k)$ the value $\dfrac{\theta}{\theta+1}\left(\dfrac{v_k}{\beta}\right)^{-\theta}$.

In consequence of this (e) becomes:

$$b \quad b_k = (b_k - b_0)\,\frac{b'_k}{1-b'_k}\,\frac{\theta+1}{\theta}\left[1-\left(\frac{v_k}{v}\right)^{\theta}\right], \quad . \quad . \quad . \quad (26)$$

in which θ is determined through (c). (c) now becomes namely:

$$\beta = \frac{b_k - b_0}{1 - b'_k}(\theta + 1)\left(\frac{v_k}{\beta}\right)^{-1},$$

yielding

$$\theta + 1 = (1 - b'_k)\,\frac{v_k}{b_k - b_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26a)$$

But here too there is no convergency for v_0, b_0. For small values of $b_k - b_0$ (26) namely approaches to

$$\frac{b_k - b_0}{b_k - b_0} = b'_k\left(\frac{v_k}{v_0}\right)^{\frac{v_k}{b_k - b_0}},$$

because $1 - b'_k$ and $(\theta + 1) : \theta$ then approach to 1, while between [ ] again 1 has been omitted by the side of $(v_k : v_0)^{\theta}$, which approaches to infinite. The first member is $=1$, the second member approaching to $0 \times a^{\infty}$, hence to ∞.

Also when $(v - v_0)^{-\theta}$ had been assumed, we should have found the same impossibility; even still intensified, because then $(v_k : v_0)^{v_k : (b_k - b_0)}$ would have become $[(v_k - v_0) : (v_0 - v_0)]^{(v_k - v_0) : (b_k - b_0)}$, because of which the root of the power would approach ∞ for all the values of $b_k - b_0$ [1]).

In the same way the functions may be tested, in which $v : (b - b_0)$ is written instead of $v : \beta$. The functions $-f'(v)$ and $f''(v)$ then become somewhat more intricate, but the divergency at v_0, b_0 continues to exist.

And as for VAN DER WAALS's equation in the general form

$$\frac{b - b_0}{v - b} = f\left[1 - \left(\frac{b - b_0}{b_g - b_0}\right)^{n}\right], \quad . \quad . \quad . \quad . \quad . \quad (27)$$

the so-called "equation of state of the molecule" — this leads to such complicated expressions for f and n, in order to satisfy the relations (24), that no physical significance can possibly be assigned to these expressions. Also when $v - v_0$ is substituted for $v - b$. We shall, therefore, enter no further into all these calculations, and leave their execution to the reader.

Before leaving this kind of functions, which all lead to failures, I will just point out that if one should want e.g. to derive from the

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[1]) Also the supposition $f(v) = \left(\frac{\beta}{v_0} - \frac{\beta}{v}\right)^{\theta} - \left(\frac{\beta}{v_0}\right)^{\theta}$ leads to the same impossibilities.

relations (24) by division, that also *outside* the critical point

$$-\frac{b''}{1-b'}=\frac{b'}{b-b_0},$$

one would easily find back (25) after integration of this differential equation. But we know that this equation does not satisfy. Also other obvious suppositions about b'' and b', which satisfy (24) at the critical point, lead to such impossible final results.

10. We have now come to the forms, which lead to possible, and at the same time not too intricate results, also as far as the convergency point v_0, b_0 is concerned. In all these forms the relation $(b-b_0):(v-v_0)$ or also $(b-b_0):(v-b)$ occurs by the side of $(b-b_0):(b_g-b_0)$. In this respect the *general* form of VAN DER WAALS's relation (27) is the best that can be assumed. Here everything is reached that can be desired. The relation $(b-b_0):(v-b)$ approaches to a finite limiting value f at $v=b=v_0$, when in the second member $b=b_0$, so that the convergency at v_0, b_0 has been properly warranted beforehand. Further b becomes $b=b_g$ for $v=\infty$. But as has been said before — in order properly to obtain the values given by (24) at v_k, *exceedingly intricate* expressions must be assigned to f and n, in which for the case $b=$ constant, i.e. b_k-b_0 or $b_g-b_0=0$ $(\gamma={}^1/_2)$ f approaches to 0 and n to ∞.

This is of course in itself nothing particular, as it is e.g. by no means necessary that, as VAN DER WAALS desires, $Lim\,(b-b_0):(v-v_0)$, is $=1$ or assumes another finite value; it can very well become $=0$, as for values of v close to v_0 (or b) b can long have assumed a value close to the limiting value b_0. This is the more apparent when we consider the case that b no longer changes at all, or hardly changes (at $\gamma={}^1/_2$). The value of b can then be put about $=b_0$ throughout its course, from $v=\infty$ to $v=v_0$, so that the numerator of $(b-b_0):(v-v_0)$ approaches much more rapidly (or infinitely more rapidly) to 0 than the denominator. Nor is a very large value for n with small values of b_k-b_0 impossible in itself.

But it is the exceeding intricacy of the expressions for f and n that make us reject equation (27) in *that* form. And these intricate results remain, so long as the exponent of $(b-b_0):(v-b)$, which is always $=1$ in (27), *differs* from that of $(b-b_0):(b_g-b_0)$, viz. n.

Let us take generally:

$$\left(\frac{b-b_0}{v-v_0}\right)^\theta=f\left[1-\left(\frac{b-b_0}{b_g-b_0}\right)^n\right], \quad \ldots\ldots \quad (27^a)$$

and let us then calculate f and n for given value of θ. It soon appears then that simplication is only found *when* $\theta = n$. The reader may be left to ascertain this fact for himself.

Accordingly we shall only treat the case that $\theta = n$ is put in (27^a) from the beginning. But first one more remark.

The equation ($27a$) is a special case of the general assumption:

$$b = b_g - (b_g - b_0)\frac{f(v)}{f(v_0)},$$

in which $f(v)$ approaches to 0 for $v = \infty$. We may, however, also write for this:

$$b - b_0 = (b_g - b_0)\left(1 - \frac{f(v)}{f(v_0)}\right),$$

or still more general:

$$\left(\frac{b - b_0}{b_g - b_0}\right)^n = 1 - \frac{f(v)}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

when $f(v_0) = Lim\, f(v)$ is denoted by a for $v = v_0$. If we now take for $f(v)$ the *special* function $[(b - b_0) : (v - v_0)]^\theta$, this passes into:

$$\left(\frac{b - b_0}{b_g - b_0}\right)^n = 1 - \frac{1}{a}\left(\frac{b - b_0}{v - v_0}\right)^\theta,$$

which corresponds with ($27a$), because a means the same thing as f. We can, therefore, consider VAN DER WAALS's form as a special case of the quite general form (28), when namely, $(b - b_0) : (v - v_0)$ is simply taken for $f(v)$, and not this ratio to a certain power, while also VAN DER WAALS substitutes $v - b$ for $v - v_0$.

But whereas VAN DER WAALS's form with $n = 2$, $\theta = 1$, $f = 1$ or more, has a physical meaning, being related to the deformation of the molecule by pressure and temperature (which deformation in our theory — see § 1 of the preceding paper — may be considered negligible, and has, therefore, been left out of account), our formula is for the present without such a significance, and it must only be considered as an *empirical* relation — just as many others, e.g. the equation of the straight diameter, that for the vapour pressure, etc. — to which possibly afterwards a physical meaning can be assigned, in relation with the different factors which give rise to a *quasi* variation of b.

So we put:

$$\left(\frac{b - b_0}{b_g - b_0}\right)^n = 1 - \frac{1}{a}\left(\frac{b - b_0}{v - v_0}\right)^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

in which $a = Lim\left(\frac{b - b_0}{v - v_0}\right)^n$ at $v = v_0$, $b = b_0$; while $b_0 = v_0$ is assumed.

If for the sake of brevity we write x for $(b-b_0):(v-v_0)$, then

$$\left(\frac{b-b_0}{b_g-b_0}\right)^n = 1 - \frac{x^n}{a},$$

which with introduction of v_k and b_k passes into

$$\left(\frac{b_k-b_0}{b_g-b_0}\right)^n = 1 - \frac{x_k^n}{a}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\alpha)$$

from which b_g can be computed, when a and n are known. Substitution yields:

$$\left(\frac{b-b_0}{b_k-b_0}\right)^n = \frac{a-x^n}{a-x_k^n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29a)$$

in which a is therefore *Lim* x_0^n. Let us derive from this the values of b' and b''. We find for b':

$$\frac{b'}{b_k-b_0}\, n \left(\frac{b-b_0}{b_k-b_0}\right)^{n-1} = -\frac{nx^{n-1}}{a-x_k^n}\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right),$$

hence for b'':

$$\frac{b''}{b_k-b_0}\, n \left(\frac{b-b_0}{b_k-b_0}\right)^{n-1} + \frac{(b')^2}{(b_k-b_0)^2}\, n\,(n-1)\left(\frac{b-b_0}{b_k-b_0}\right)^{n-2} =$$

$$= -\frac{n\,(n-1)\,x^{n-2}}{a-x_k^n}\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right)^2 -$$

$$-\frac{n\,x^{n-1}}{a-x_k^n}\left[2\frac{b-b_0}{(v-b_0)^3} - 2\frac{b'}{(v-b_0)^2} + \frac{b''}{v-b_0}\right].$$

Hence at the critical point after multiplication by b_k-b_0, resp. $-(b_k-b_0)^2$:

$$\left.\begin{array}{l} b'_k = x_k^{n-1}\,\dfrac{x_k^2 - b'_k\, x_k}{a-x_k^n} \quad ; \quad -b''_k\,(b_k-b_0) - (n-1)\,(b'_k)^2 = \\[2ex] = \dfrac{(n-1)\,x_k^{n-2}\,(x_k^2-b'_k\,x_k)^2 + x_k^{n-1}\,[2x_k^3-2b'_k\,x_k^2 + b''_k\,(b_k-b_0)\,x_k]}{a-x_k^n} \end{array}\right\}.$$

The first equation yields at once:

$$b'_k\left(1+\frac{x_k^n}{a-x_k^n}\right) = \frac{x_k^{n+1}}{a-x_k^n},$$

hence $b'_k \,.\, a = x_k^{n+1}$, or

$$a = \frac{x_k^{n+1}}{b'_k}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (\beta)$$

The second gives:

$$-\,b''_k\,(b_k-b_0)\left(1+\frac{x_k^n}{a-x_k^n}\right) - (n-1)\,(b'_k)^2 =$$

$$= \frac{(n-1)(b'_k)^2 x_k^n - 2(n-1)b'_k\,x_k^{n+1} - 2b'_k\,x_k^{n+1} + (n-1)x_k^{n+2} + 2x_k^{n+2}}{a-x_k^n},$$

hence:

$$-b''_k(b_k-b_0)a-(n-1)(b'_k)^2(a-x_k^n)=(n-1)(b'_k)^2x_k^n-2nb'_k\,x_k^{n+1}+(n+1)x_k^{n+2}.$$

As according to (24) $-b''_k\,(b_k-b_0)=(b_k-b_0)^2\,(1-b'_k):b_k\,v_k$, i. e. $=b'_k\,(1-b'_k)$, we have also:

$$[b'_k-(b'_k)^2]\,a=(n-1)\,(b'_k)^2\,a-2nb'_k\,x_k^{n+1}+(n+1)\,x_k^{n+2},$$

or

$$n\,(b'_k)^2\,a-b'_k\,a-2n\,b'_k\,x_k^{n+1}+(n+1)\,x_k^{n+2}=0.$$

After substitution of x_k^{n+1} for b'_ka, and division by x_k^{n+1}, we get:

$$nb'_k-1-2n\,b'_k+(n+1)\,x_k=0,$$

or

$$(n+1)\,x_k-nb'_k=1,$$

from which

$$n=\frac{1-x_k}{x_k-b'_k}\quad\ldots\ldots\ldots\ldots\quad(\gamma)$$

On account of the value found for a, we can now write for (29a):

$$\left(\frac{b-b_0}{b_k-b_0}\right)^n=\frac{x_k^{n+1}-b'_k\,x^n}{x_k^{n+1}-b'_k\,x_k^n},$$

or also

$$\underline{\left(\frac{b-b_0}{b_k-b_0}\right)^n=\frac{x_k-b'_k\left(\dfrac{x}{x_k}\right)^n}{x_k-b'_k}},\quad\ldots\ldots\quad(30)$$

in which

$$\underline{x=\frac{b-b_0}{v-b_0}}\;;\quad\underline{x_k=\frac{b_k-b_0}{v_k-v_0}}\;;\quad\underline{b'_k=\frac{(b_k-b_0)^2}{b_k\,v_k}}\;;\quad\underline{n=\frac{1-x_k}{x_k-b'_k}},\quad.\quad(30a)$$

while from (α), (β) taken into consideration, follows:

$$\underline{\left(\frac{b_k-b_0}{b_g-b_0}\right)^n=1-\frac{b'_k}{x_k}}\quad;\quad\underline{x_0^{\,n}=a=\frac{x_k^{n+1}}{b'_k}}\quad\ldots\quad(30b)$$

11. It is easily seen that the found equation (30) fulfils all conditions. In the first place we get properly

$$\left(\frac{b_g-b_0}{b_k-b_0}\right)^n=\frac{x_k}{x_k-b'_k},$$

for $v=\infty$ ($x=0$), which is in harmony with (30^b). Secondly the first member $=1$ for $v=v_k$ ($x=x_k$), the second member $(x_k-b'_k):(x_k-b'_k)$ also becoming $=1$. Thirdly for $b=b_0$, $v=v_0$ the first member $=0$, and the numerator of the second member $=x_k-\dfrac{b'_k\,a}{x_k^n}$, as $x_0^{\,n}=a$ is put. But $b'_k\,a=x_k^{n+1}$, hence this numerator is also $=0$.

By differentiation of (30), considering that there b'_k stands for

$(b_k - b_0)^2 : b_k v_k$, which we shall call β for a moment, we find further:

$$n\left(\frac{b-b_0}{b_k-b_0}\right)^{n-1}\frac{b'}{b_k-b_0}=\frac{1}{x_k-\beta}\left(-\frac{\beta}{x_k^n}nx^{n-1}\right)\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right),$$

which becomes for v_k:

$$b'_k=\frac{\beta}{x_k(x_k-\beta)}(x_k^2-b'_k x_k)=\beta\frac{x_k-b'_k}{x_k-\beta},$$

from which immediately follows $b'_k=\beta$, i.e. the value given by (24). And with regard to b''_k, from

$$-\frac{b'}{b_k-b_0}\left(\frac{b-b_0}{b_k-b_0}\right)^{n-1}=\frac{\beta}{x_k^n(x_k-\beta)}x^{n-1}\left(-\frac{b-b_0}{(v-b_0)^2}+\frac{b'}{v-b_0}\right) \qquad (a)$$

follows after a second differentiation, and substitution of $v=v_k$ and $b=b_k$ (see also above):

$$-b''_k(b_k-b_0]-(n-1)b'^2_k=\frac{\beta}{x_k^n(x_k-\beta)}\Big[(n-1)x_k^{n-2}(x_k^2-b'_k x_k)^2+$$

$$+x_k^{n-1}[2x_k^3-2b'_k x_k^2+b''_k(b_k-b_0)x_k]\Big],$$

yielding, when β is written for b'_k:

$$-b''_k(b_k-b_0)\left(1+\frac{\beta}{x_k-\beta}\right)=(n-1)\beta^2+\beta\Big[(n-1)(x_k-\beta)+2x_k\Big],$$

or

$$-b''_k(b_k-b_0)x_k=\beta(x_k-\beta).(n+1)x_k.$$

Now according to (30^a) $(n+1)(x_k-\beta)=(1-x_k)+(x_k-\beta)=1-\beta$; hence

$$-b''_k(b_k-b_0)=\beta(1-\beta)=b'_k(1-b'_k),$$

and now (24) is again satisfied.

After having thus carried out these control calculations, we return to equation (30).

The quantity b'_0 cannot be computed from the above equation (a) for b', as the latter gives $0=0$ for v_0, b_0. No more could b''_0 be calculated from the general equation for b''. But since in the neighbourhood of v_0, b_0:

$$x=\frac{b-b_0}{v-v_0}=b'_0+{}^1/_2\, b''_0(v-v_0)+\ldots$$

evidently $b'_0=Lim\dfrac{b-b_0}{v-v_0}=x_0$, and hence according to (30b) $=\sqrt[n]{a}$.

When we represent $(b-b_0):(b_k-b_0)$ by δ,

$$b'_0\delta^{n-1}=\frac{\beta}{x_k^n(x_k-\beta)}x^{n-1}\left(\frac{x^2}{\delta}-\frac{b'_0 x}{\delta}\right)$$

follows from the above equation (α) for b'; or also, since x^n approaches $x_0{}^n = a = x_k{}^{n+1} : b'_k$, and $\beta = b'_k$:

$$b'_0 \delta^n = \frac{x_k}{x_k - b'_k} (x - b'_0) .$$

Now $x - b'_0 = {}^1\!/_2\, b''_0 (v - v_0)$, hence:

$$b''_0 = 2 b'_0 \delta^n \, \frac{x_k - b'_k}{x_k} \, \frac{1}{v - v_0} ,$$

or also

$$b''_0 (b_k - b_0) = 2 (b'_0)^2 \delta^{n-1} \, \frac{x_k - b'_k}{x_k} ,$$

since $(b_k - b_0) : (v - v_0) = ((b_k - b_0) : (b - b_0)) \times ((b - b_0) : (v - v_0)) = \delta^{-1} \times b'_0$.

With assumption of (30) the value of b''_0 is therefore always $= 0$, since δ approaches to 0. The final course of the curve $b = f(v)$ is therefore straight, the coefficient of direction being indicated by $b'_0 = \sqrt[n]{a}$.

That for $v = \infty$, in consequence of $v - v_0$ in the numerator of x, both b'_g and b''_g become $= 0$, is self-evident.

Let us now examine the values of a and n for different values of $b_k - b_0$ or of γ.

When we substitute in $n = (1 - x_k) : (x_k - b'_k)$ the values of x_k and b'_k, we get:

$$n = \frac{1 - \dfrac{b_k - b_0}{v_k - v_0}}{\dfrac{b_k - b_0}{v_k - v_0} - \dfrac{(b_k - b_0)^2}{b_k v_k}} ,$$

or also, taking the relations (22) into account, i. e. $b_k : b_0 = 2\gamma$, $v_k : v_0 = 2(1 + \gamma)$, in which $b_0 = v_0$:

$$n = \left(1 - \frac{2\gamma - 1}{2\gamma + 1}\right) : \left(\frac{2\gamma - 1}{2\gamma + 1} - \frac{(2\gamma - 1)^2}{4\gamma(\gamma + 1)}\right) ,$$

i. e.

$$n = 8\gamma(\gamma + 1) : (2\gamma - 1) \Big[4\gamma(\gamma + 1) - (2\gamma + 1)(2\gamma - 1) \Big] ,$$

or

$$n = \frac{8\gamma(\gamma + 1)}{(2\gamma - 1)(4\gamma + 1)} = \frac{2 b_k v_k}{(b_k - b_0)(2 b_k + b_0)} \quad . \quad . \quad . \quad (31)$$

So the exponent n ranges from $3^1\!/_5$ (when $\gamma = 1$) to ∞ (when $\gamma = {}^1\!/_2$). For ordinary substances ($\gamma = 0{,}9$) n becomes $= 46 : 171 = 3{,}72$; for Argon ($\gamma = 0{,}75$) $n = 5{,}25$.

For the value of a, i. e. the limiting value x_0 of $(b-b_0):(v-v_0)$ for $v=v_0$, $b=b_0$, we find from $x_0{}^n = a = x_k{}^{n+1} : b'_k$ (see 30^b) the value:

$$x_0 = \sqrt[n]{a} = x_k \sqrt[n]{\frac{x_k}{b'_k}} = \frac{2\gamma-1}{2\gamma+1} \sqrt[n]{\frac{4\gamma(\gamma+1)}{4\gamma^2-1}}, \quad . \quad . \quad (32)$$

in which n possesses the value given by (31). This limiting value x_0, which is at the same time $= b'_0$ (see above) assumes for $\gamma=1$ the value:

$\frac{1}{3}\sqrt[3^1/_5]{\frac{8}{3}} = {}^1/_3 \times 1{,}359 = 0{,}453$; for $\gamma = 0{,}9$ the value $\frac{0{,}8}{2.8}\sqrt[3{,}72]{\frac{6.84}{2.24}} = {}^2/_7 \times 1{,}350 = \underline{0{,}386}$; for $\gamma=0{,}75$ the value $\frac{0{,}5}{2{,}5}\sqrt[5^1/_4]{\frac{5{,}25}{1{,}25}} = {}^1/_5 \times 1{,}314 = 0{,}263$; while for $\gamma = 0{,}5$ it properly approaches 0 ($b-b_0$ then namely has become continually $=0$). For $\sqrt[n]{(x_k:b'_k)}$ then approaches unity, the factor $(2\gamma-1):(2\gamma+1)$ approaching to 0.

Accordingly for all "ordinary substances", where γ is about 0,9, the line $b=f(v)$ will approach the point of convergency v_0, b_0 at an angle of about 21° ($tg\,\varphi = 0{,}39$).

In conclusion we will still discuss the value of $b_g : b_k$ according to (30^b), viz.

$$\frac{b_g-b_0}{b_k-b_0} = \sqrt[n]{\frac{x_k}{x_k-b'_k}}.$$

The limiting value of this for $\gamma=1$ is evidently $\sqrt[3^1/_5]{\left[{}^1/_3 : ({}^1/_3 - {}^1/_8)\right]} = \sqrt[3^1/_5]{1{,}6} = 1{,}158$, which with $b_k : b_0 = 2$ leads to $b_g : b_k = 1{,}079$.

For ordinary substances ($\gamma = 0{,}9$) we find $\sqrt[3{,}72]{\left[{}^2/_7 : ({}^2/_7 - {}^8/_{85{,}5})\right]} = \sqrt[3{,}72]{(171 : 115)} = 1{,}113$, leading with $b_k : b_0 = 1{,}8$ to $b_g : b_k = \underline{1{,}050}$, i. e. the normal value. For Argon ($\gamma = 0{,}75$) the second member becomes $\sqrt[5{,}25]{\left[{}^1/_5 : ({}^1/_5 - {}^1/_{21})\right]} = \sqrt[5{,}25]{(21:16)} = 1{,}053$, which with $b_k : b_0 = 1{,}5$ for $b_g : b_k$ yields the value 1,018. Finally for an ideal substance $b_g : b_k = 1$.

Equation (30) found by us, therefore, yields good results in every respect, from $v=\infty$ to $v=v_0$, and that for all values of $b_k - b_0$ or of γ. In addition it may once more be stated, that when $b=b_0$ in the first member, the second member too must be $=0$, hence $x_k = b'_k\,(x_0 : x_k)^n$, in consequence of which $a = x_0{}^n$ assumes the value

$x_k^{n+1} : b'_k$, thus properly the value given by (30^b). It is also easy to see that in the limiting case $\gamma = {}^1/_2$, i.e. $b_k = b_0$, the equation (30) passes into $b = const. = b_0$. For then $b'_k = 0$, and the second member becomes constantly $= 1$, i.e. b constant $= b_k = b_0$.

12. It is self-evident that the equation (30) is not the only one that will satisfy the different conditions. Thus in the second member of (29) e. g. we might have assumed $v - b$ in the denominator instead of $v - v_0$. A calculation quite analogous to that in § 10 would then again have enabled us to find a set of values for n and a. But then they would have been less simple than with $v - v_0$. It is easily seen that the result is obtained by substituting $(1 + b'_k) : (1 - b'_k)$ in $n = (1 - x_k) : (x_k - b'_k)$ for unity, and $b'_k : (1 - b'_k)$ for b' [1]), so that we then get:

$$n = \left(\frac{1+b'_k}{1-b'_k} - x_k\right) : \left(x_k - \frac{b'_k}{1-b'_k}\right); \quad x_0 = \sqrt[n]{a} = x_k \sqrt[n]{\frac{x_k}{b'_k : (1-b'_k)}},$$

having

$$\frac{b_g - b_0}{b_k - b_0} = \sqrt[n]{\frac{x_k}{x_k - b'_k : (1 - b'_k)}}$$

The equation $b = f(v)$ itself becomes:

$$\left(\frac{b - b_0}{b_k - b_0}\right)^n = \frac{x_k - \frac{b'_k}{1 - b'_k}\left(\frac{x}{x_k}\right)^n}{x_k - b'_k : (1 - b'_k)}.$$

But when we now wish to express n in γ we get, instead of $n = 8\gamma(\gamma + 1) : (2\gamma - 1)(4\gamma + 1)$ according to (31), the less satisfactory expression $(10\gamma + 1) : (2\gamma - 1)(4\gamma + 1)$, in which $10\gamma + 1 = 5b_k + b_0) : b_0$ has a much less simple signification than $8\gamma(\gamma + 1) = b_k v_k : b_0^2$. We remind of the fact that x_k is now $= (b_k - b_0) : (v_k - b_k)$, hence $= (2\gamma - 1) : 2$.

And there will be no doubt that more such functions are to be found, which lead to more or less complicated expressions — but we confine ourselves to the above.

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[1]) For where we found above $b'_k = x_k^{n-1} \times (x_k^2 - b'_k x_k) : (a - x_k^n)$, a factor $1 - b'_k$ will now occur by the side of x_k^2, so that after division of both members by $1 - b'_k$ everywhere b'_k has been replaced by $b'_k : (1 - b'_k)$. And in the equation for b''_k, $[b'_k - (b'_k)^2]\, a$ in the first member will be replaced by $(b'_k - (b'_k)^2)(a + x_k^{n+1}) : (1 - b'_k)^2$, when both members are now divided by $(1 - b'_k)^2$. On account of this $b'_k : (1 - b'_k)$ comes everywhere in the second member, where b'_k stood before, while in the first member $(b'_k - (b'_k)^2) \times (a + x_k^{n+1})$, is substituted for $(b'_k - (b'_k)^2)\, a$, the consequence of which is that, after application of entirely the same reductions as above, $nb'_k - 1 - 2nb'_k + (n + 1)\, x_k = 0$ is replaced by $nb'_k : (1 - b'_k) - (1 + b'_k) : (1 - b'_k) - 2nb'_k : (1 - b'_k) + (n + 1)\, x_k = 0$.

In our concluding paper something will be said about the temperature influence, which will manifest itself by continual diminution of $b_k - b_0$, at first slowly, then more rapidly, as the absolute zero is approached. Descending from high to low temperatures one can therefore pass through all the types. If the critical region of a substance lies in the region of low temperatures, the critical quantities, and also the isotherms in the neighbourhood of the critical point, will present, as far as the course of b is concerned, the little variable type with slight $b_k - b_0$ (γ in the neighbourhood of 0,5). But these same substances will of course show the same variability of b as the "ordinary" substances at high temperatures. Reversely the ordinary substances, considered at low temperatures, will assume the Argon-, Hydrogen- or Helium-type, with respect to the slight variability of b at these temperatures. Etc. Etc.

In this concluding paper I shall also communicate the b-values for Argon I have calculated; besides I shall venture to give some theoretical considerations concerning the diminution of the factor 4 in $b_g = 4m$ with fall of the temperature.

Fontanivent sur Clarens, February 1914.

Mathematics. — "*The envelope of the osculating ellipses, which are described by the representative point of a vibrating mechanism having two degrees of freedom of nearly equal frequencies.*"

By H. J. E. BETH. (Communicated by Professor D. J. KORTEWEG).

(Communicated in the meeting of February 28, 1914).

§ 1. In my paper on the small oscillations of mechanisms with two degrees of freedom [1]), LISSAJOUS curves with their envelopes were discussed, which envelopes form the boundaries of the domain of motion. In a summarizing treatment of a more general problem [2]) my further inquiries as to these envelopes have also been included. These inquiries were extended over a system of LISSAJOUS curves, more general than the system which is of importance for the dynamical problem. However the envelopes were considered exclusively from a dynamical point of view, so that purely geometrical properties together with the shape of the curves outside the domain of motion remained unknown. Moreover what came to light about the shape of the envelope remained for the greater part restricted to simple cases, e.g. in the case, formerly indicated by $S=2$, to the symmetrical case, as quoted, indicated by $p+q=0$, $l=0$.

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[1]) These Proceedings pp. 619—635 and 735—750 (1910).

[2]) Phil. Mag., sixth series Number 152 (1913).

In what follows for $S=2$, the case of the equality of frequencies, the envelope will be treated anew and from a more geometrical point of view.

We shall therefore have to occupy ourselves with the envelope (L) of the system of ellipses

$$x=\sqrt{\zeta}\cos t \quad , \quad y=\sqrt{1-\zeta}\cos(t-\varphi).$$

in which ζ and φ are two variable quantities in the most general case connected by the relation:

$$\sqrt{\zeta(1-\zeta)}\cos\varphi=-\frac{1}{2}l\pm\sqrt{p\zeta^2+q\zeta+r+\frac{1}{4}l^2}.$$

By elimination of t we find for the equation of the ellipses

$$(A) \qquad (1-\zeta)x^2-2\sqrt{\zeta(1-\zeta)}\cos\varphi\,.\,xy+\zeta y^2=\zeta(1-\zeta)\sin^2\varphi.$$

Let us now determine the reciprocal polar curves of these ellipses with respect to the circle:

$$(C) \qquad x^2+y^2=1,$$

in the circumference of which circle the vertices are situated of the rectangles, which are circumscribed to the ellipses (A), and have their sides parallel with the axes. The envelope (L') of this new system of ellipses will be the reciprocal polar curve of the envelope (L) wanted. (Cf. note p. 943).

The new system of ellipses appears to be given by:

$$(A') \qquad \zeta x^2+2\sqrt{\zeta(1-\zeta)}\cos\varphi\,.\,xy+(1-\zeta)y^2=1.$$

By elimination of φ between this equation and the given relation between ζ and φ we find:

$$4\left(p\zeta^2+q\zeta+r+\frac{1}{4}l^2\right)x^2y^2=\{1-\zeta x^2+lxy-(1-\zeta)y^2\}^2.$$

This equation contains ζ to a no higher order than two. The equation of the envelope of (A') may consequently be written down at once. After some reduction this equation of (L') becomes:

$$-(4r+l^2)(y^2-x^2)^2-4p(1+lxy-y^2)^2+4p(4r+l^2)x^2y^2=$$
$$=4q^2x^2y^2-4q(1+lxy-y^2)(y^2-x^2).$$

As (L') is now apparently of the fourth order, *the envelope (L) wanted is of the fourth class.*

As (L') in general as we shall see, has no double points or cusps, it has been determined by this, that (L) *is of the twelfth order.*

(L), like (L'), has the origin as centre.

If we multiply the equation found for (L') by p, (the cases $p=0$ and $p=\infty$ we shall consider separately in § 9) it appears that it may be written thus:

$$(L') \qquad \{qx^2+2plxy-(2p+q)y^2+2p\}^2 = s\{x^4-2(2p+1)x^2y^2+y^4\},$$

where

$$s \equiv q^2 - p\,(4r + l^2).$$

§ 2. It is evident from the equation just found that out of the origin 4 bitangents may be drawn to (L'), given by

$$x^4 - 2\,(2p + 1)\,x^2y^2 + y^4 = 0.$$

The 8 points of contact are lying on the conic

$$(K) \qquad qx^2 + 2plxy - (2p + q)y^2 + 2p = 0.$$

The bitangents are real or imaginary, according to p being positive or negative. They form two pairs of perpendicular lines, lying symmetrically with regard to the axes and with regard to the straight lines that bisect the angles of the axes.

If (K) has its axes along the axes of coordinates or along the bisectrices, then (L') and consequently (L) as well will have those lines as lines of symmetry. The first occurs for $l = 0$, the second for $p + q = 0$. These two suppositions consequently give rise to the same simplification in the shape of (L). In the formerly amply discussed case that $l = 0$ as well as $p + q = 0$, (K) becomes a circle with $\sqrt{2}$ as radius.

§ 3. *Nodes of* (L). Let us write the equation of (L') found in § 1 in the shape

$$U^2 = MN,$$

in which

$$U = \frac{qx^2 + 2plxy - (2p + q)y^2 + 2p}{\sqrt{s}}$$

and M and N are expressions of the second order, obtained by separation of the expression $x^4 - 2(2p + 1)x^2y^2 + y^4$, then we see, that (L') is touched in 4 points by each conic of the system,

$$\lambda^2 M + 2\lambda U + N = 0,$$

in which λ represents a parameter.

The separation of the expression mentioned, may be executed in the following ways:

$$\begin{aligned} x^2-2(2p+1)x^2y^2+y^4 &= (x^2+2\sqrt{p}\,xy-y^2)(x^2-2\sqrt{p}\,xy-y^2) \\ &= (x^2+2\sqrt{p+1}\,xy+y^2)(x^2-2\sqrt{p+1}\,xy+y^2) \\ &= \{x^2-(\sqrt{2p+1}-2\sqrt{p(p+1)})y^2\}\{x^2- \\ &\qquad -(\sqrt{2p+1}+2\sqrt{p(p+1)})y^2\}. \end{aligned}$$

The first way of separation leads to the following system of inscribed conics

$$\left(\lambda^2 + 2\frac{q}{\sqrt{s}}\lambda + 1\right)x^2 + 2\left(\lambda^2 + l\sqrt{\frac{p}{s}}\lambda - 1\right)xy - \left(\lambda^2 + \right.$$
$$\left. + 2\frac{2p+q}{\sqrt{s}}\lambda + 1\right)y^2 = -\frac{4p}{\sqrt{s}}\lambda.$$

The values of λ, other than 0 or ∞, for which this equation represents a degeneration, viz. a degeneration into two parallel straight lines, are determined by the equation:

$$\left(\lambda^2 + l\sqrt{\frac{p}{s}}\lambda - 1\right)^2 + \left(\lambda^2 + 2\frac{q}{\sqrt{s}}\lambda + 1\right)\left(\lambda^2 + 2\frac{2p+q}{\sqrt{s}}\lambda + 1\right) = 0.$$

Each of the straight lines of a degeneration touches (L') in two points, is therefore a bitangent of (L'). If we write the equation of such a straight line in the shape

$$ax + by = 1,$$

then we see easily that we have

$$a^2 + b^2 = 1,$$

i.e. the 4 pairs of parallel bitangents touch (C).

We may observe that the system of conics to which we have arrived is the system of ellipses (A') itself, which is apparent, if we replace the parameter ζ by λ, in such a way that:

$$4p\zeta^2 + 4q\zeta + 4r + l^2 = \frac{q^2 - 4pr - pl^2}{4p}\left(\lambda - \frac{1}{\lambda}\right)^2.$$

Let us proceed now to the second way of separation. The equation of the second system of inscribed conics and the equation determining the degenerations may be written down. So we come again to 4 pairs of parallel bitangents of (L'); they appear to touch the hyperbola:

$$x^2 - y^2 = -\frac{p}{p+q}.$$

In the same way the third method of separating leads to 4 pairs of parallel bitangents of (L'), which touch the hyperbola

$$xy = -\frac{1}{2l}.$$

Hence:

Of the 28 bitangents which the envelope (L'), possesses 4 pass through O; the remaining ones are pairs of parallel lines; 8 of them touch the circle $x^2 + y^2 = 1$, 8 the hyperbola $x^2 - y^2 = -\dfrac{p}{p+q}$, and 8 the hyperbola $xy = -\dfrac{1}{2l}$.

We now transfer what we have found to (L):

Of the 28 *nodes of the envelope* (L), 4 *are lying at infinity,* 8 *on the circumference of the circle* $x^2+y^2=1$, 8 *on the hyperbola* $x^2-y^2=-\frac{p+q}{p}$ *and* 8 *on the hyperbola* $xy=-2l$.

The 4 pairs of parallel asymptotes of (L), which correspond with the bitangents of (L') passing through O, touch the conic (K'), which is the reciprocal polar curve of (K).

The nodes of (L) lying on (C), if they are real, are for the dynamical problem under discussion the vertices of the quadrangular figures, which as appeared before, may serve as envelopes; the branches intersecting in those points meet perpendicularly, as was proved for a more general case [1]).

§ 4. *Asymptotes of* (L). Besides the 4 pairs of parallel asymptotes, (L) has moreover generally speaking 4 asymptotes passing through O, which are perpendicular to the asymptotes of (L').

Of (L') two asymptotical directions may coincide.

In this case the corresponding asymptotes do not pass through O, but they are removed from O at equal distances. In that case on the straight lines passing through O (L) has two cusps in which the straight line is a tangent. The said straight line is to be considered to belong to (L); consequently (L) is degenerate.

Various shapes of (L').

§ 5. The equation of (L') reads (§ 1):

$$\{qx^2+2plxy-(2p+q)y^2+2p\}^2=s\{x^4-2(2p+1)x^2y^2+y^4\},$$

where

$$s\equiv q^2-p(4r+l^2).$$

Its shape will in the first place be dependent on the nature of the bitangents drawn from O, viz. whether they are imaginary $(p<0)$, or real $(p>0)$ and touch the curve in real points or are isolated.

Further on the nature of the conic (K) which may be an ellipsis, an hyperbola or a degeneration.

Finally on the reality of the asymptotes.

We can prove now, that (L') *has as many real asymptotical directions as it has pairs of real points of intersection with* (C).

Let $(\cos\alpha, \sin\alpha)$ be the point of (C) lying on (L'), then we have:

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[1]) Phil. Mag. l. c., p. 297.

ibed by the

H. J. E. BETH. [illegible] freedom of nearly equal frequencies."

Fig. 1

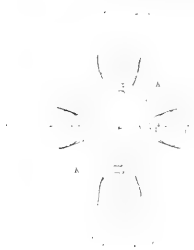

Fig. 2

Fig. 3

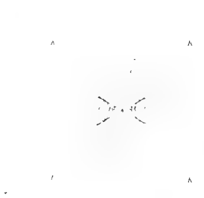

Fig. 4

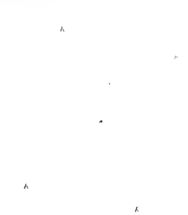

Fig. 5

Fig. 6

Fig. 7

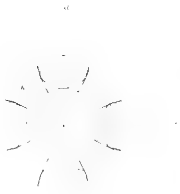

Fig. 8

Fig. 9

Fig. 10

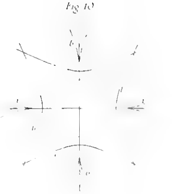

Fig. 11

Fig. 12

Fig. 13

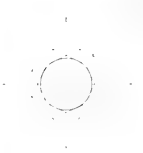

Fig. 14

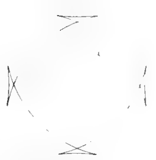

Fig. 15

Fig. 16

Fig. 17

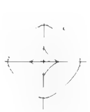

Fig. 18

Fig. 19

Fig. 20

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$$\{q\cos^2\alpha + 2pl\cos\alpha\sin\alpha - (2p+q)\sin^2\alpha + 2p\}^2 =$$
$$= s\{\cos^4\alpha - 2(2p+1)\cos^2\alpha\sin^2\alpha + \sin^4\alpha\}.$$

If we write this in the form:

$$\{q\sin^2\alpha - 2pl\cos\alpha\sin\alpha - (2p+q)\cos^2\alpha\}^2 =$$
$$= s\{\sin^4\alpha - 2(2p+1)\cos^2\alpha\sin^2\alpha + \cos^4\alpha\}$$

then it is evident, that

$$y = -x\,cotg\,\alpha$$

in an asymptotical direction of (L').

If (L') touches (C), two asymptotical directions coincide, they are perpendicular to the line that connects O with the points of contact.

§ 6. (K) *is an ellipsis.*

1°. $p > 0$, consequently the bitangents from O are real. They cut (K) in real points, in which points they touch (L').

The bitangents divide the plane into 8 angles, in which

$$H_4 \equiv x^4 - 2(2p+1)x^2y^2 + y^4$$

is alternately positive and negative. (L') lies for positive values of

$$s \equiv q^2 - p(4r + l^2)$$

in the angles, where H_4 is positive.

Let us call the branches of (L'), which are lying in the one pair of opposite angles, a, those which are situated in the other pair, b.

Let us begin by giving positive values to s and let us first consider a exclusively.

For $s = \infty$ degeneration in two bitangents. For large values of s, a consists of one branch with two asymptotes and four points of inflexion. For decreasing values of s the angle between the asymptotes becomes smaller, the apices are removed from each other and the points of inflexion move towards infinity. For a definite value of s the asymptotes are parallel. If there is a further decrease in s, a will consist of two closed branches in which for another special value of s points of osculation occur in the sides turned towards O. Then two points of inflexion appear in each branch and the branches contract, till we have for $s = 0$ degeneration in the ellipsis (K) [1].

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[1] The case $s \equiv q^2 - p(4r + l^2) = 0$ must be inquired into separately. For $s = 0$ is the condition that in the second part of the relation between ζ and φ (p. 939) the root may be drawn. In this case (A') represents two *pencils* of ellipses. Consequently the required envelope (L) has now degenerated into 8 straight lines, which are the polar lines of the base points of those pencils, and in (K'), which is the polar curve of (K).

If we allow s to change from ∞ into 0, b passes through an equal change of shape. If we consider a and b, however, together, then the general and special values of s, for which two asymptotical directions coincide, and those for which points of osculation occur, will not be the same for a and b.

If we take into consideration what has been observed in § 5 with respect to the asymptotical directions of (L') and its points of intersection with (C), it is evident that we have to distinguish the following cases, which are represented in fig. 1 (with the exception of the 3rd):

1. a and b both cut (C); they have each two intersecting asymptotes.

2. a touches (C), b cuts (C); a has two intersecting, b two parallel asymptotes.

3. a lies outside (C), b cuts (C); a has two intersecting asymptotes, b consists of closed branches.

4. a lies outside (C), b touches (C); a has two parallel asymptotes, b consists of closed branches.

5. a and b lie both outside (C); both consist of closed branches.

In this we have not yet paid attention to the presence or absence of the points of inflexion in the closed branches; the number of cases would be increased by this.

It is evident that a value of s exists, below which points of inflexion occur both in the closed branches a and b. In that case all the 28 bitangents of (L') are real.

We have now allotted to s all positive values, for negative values of s (L') lies in the other four angles. If we revolve the system of axes 45°, we shall get the same cases again.

The value of p determines the situation of the bitangents drawn from O. For increasing values of p they move towards the axes, for decreasing values of p towards the lines that bisect the axes-angles. We shall have to consider the limit-cases separately.

§ 7. 2°. $p < 0$, consequently the bitangents from O are imaginary.

For a very great value of s (which we have always to take positive here) (L') consists of a small closed branch, given by

$$x^4 - 2(2p+1)x^2y^2 + y^4 = \frac{4p^2}{s},$$

symmetrical with regard to the axes and the bisectrices. It possesses

8 points of inflexion or none, according to p being $< -\frac{1}{2}$ or $> -\frac{1}{2}$.

We shall suppose $p > -1$. This is sufficient, for it is easy to prove that (L') for a value of $p < -1$ by revolving the system of axes 45° passes into a curve answering to a value of $p > -1$.

If s decreases, the closed branch will increase while the symmetry is lost. For a certain value of s it touches (C) in two points. Then it cuts (C) in four points, in consequence of which according to the observations made in § 5, infinite branches occur. For a smaller value of s the closed branch which we shall call a, again touches (C) internally in two points. Then a cuts (C) in 8 points while new infinite branches appear. If s decreases further, then a touches (C) externally in two points; two asymptotes of b become parallel. Further a cuts (C) moreover in 4 points while two asymptotes of b have become imaginary. After this external touching occurs again, after which a has quite passed outside (C). At the same time b has become a closed branch. All the time a has remained inside (K), b outside (K), for (L') cannot cut (K) now as H_4 cannot become zero. It is evident, that, if (L') has assumed the form of a ring, a must have lost its points of inflexion if it possessed them. They will have disappeared with four at a time. After the falling together of two asymptotical directions, points of inflexion will occur in b so that the closed branch b may possess 8 points of inflexion. On further decrease of s these points of inflexion will disappear by four at a time, while the branches a and b approach each other, in order to coincide with (K) for $s = 0$.

In Fig. 2 (L') is represented for a certain value of $p < 0$ (viz. $< -\frac{1}{2}$) for some values of s.

From the equation of (L') appears at once that for $p = -1$, (L') has degenerated into two conics; at the same time (L) has degenerated into two conics.

In the figures (K) and (C) have not been drawn as intersecting; it is easily shown that they cannot intersect each other if (K) is an ellipsis.

§ 8. (K) *is an hyperbola.*

1°. $p > 0$, so the bitangents from O are real.

From the equation of (K) we deduce easily that the angle of the asymptotes is always greater than 90°. Hence (K) will cut at least

2 of the bitangents from O. Of the 4 bitangents 0, 1 or 2 are consequently isolated.

Fig. 3 refers to the case that two of the bitangents are isolated. For a few positive and negative values of s, (L') has been drawn.

Fig. 4 refers to the case that 1 bitangent is isolated.

Fig. 5 to the case that none of the bitangents is isolated; (L') therefore touches the 4 bitangents drawn from O in real points.

2°. $p < 0$, so the bitangents from O are imaginary.

Fig. 6 gives a representation of this (p is supposed $> -\frac{1}{2}$).

(In the figures (K) and (C) are represented as intersecting; this is indeed always the case if (K) is an hyperbola).

(K) is a degeneration.

As $p \neq 0$ is supposed, we have only to consider the case of degeneration in two parallel lines that touch (C). Generally speaking we can say that substantially everything is as when (K) is an hyperbola. If the bitangents are real they will generally touch (L') in real points.

§ 9. *Special cases $p = 0$ and $p = \infty$.* These cases had to be considered separately (§ 1).

For $p = 0$ and $q \neq 0$ the first equation which we have found in § 1 for (L') passes into:

$$+ (4r + l^2)(y^2 - x^2)^2 + 4q^2 x^2 y^2 + 4q(1 + lxy - y^2)(y^2 - x^2) = 0.$$

If we write:

$$\frac{4r + l^2}{4q} = t,$$

then the equation becomes:

$$\{tx^2 + lxy - (t + 1)y^2 + 1\}(y^2 - x^2) = qx^2y^2,$$

(L') has now a node in O. For the rest various cases may occur also here, which we are not going to consider separately.

If $p = 0$ and besides $q = 0$, then we have to consider the problem separately (cf. note p. 143). It is evident then that (L) consists of two rectangles [1]).

For $p = \infty$ and $q \neq \infty$, the first equation of (L') found in § 1 represents two hyperbolae, intersecting in the points $(0, \pm 1)$; $p = \infty$ involves, according to the relation between ζ and φ (§ 1), $\zeta = 0$. There is therefore no question of an envelope (L'). For $p = \infty$ and at the same time $q = \infty$ the envelope must be found again. It appears that (L) consists of 2 rectangles [2]).

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[1]) Phil. Mag. p. 315.

[2]) Phil. Mag. p. 315.

Various shapes of the envelope (L).

§ 10. The number of various shapes which (L') and consequently also (L) may assume is, as we have deduced in what precedes, very great. In order to facilitate the survey of those various forms, we shall begin with the case that $p+q=0$ and at the same time $l=0$. The equation of (L') runs:

$$q^2(x^2+y^2-2)^2 = s\{x^4-2(1-2q)x^2y^2+y^4\} \qquad (s=q^2+4qr).$$

The equations of the 4th order in λ as mentioned in § 3 are now of a quadratic form. The situation of the double points of (L) may therefore be determined by means of quadratic equations; of the double points 8 are lying on the axes, 8 on the bisectrices. The cases $q=0$ and $q=\infty$ have been considered separately (§ 9).

For an arbitrary value of q we have besides the values $s=0$ and $s=\infty$, for which (L') degenerates, two more special values of s, viz. a value for which the asymptotical directions coincide in pairs and one for which the points of inflexion coincide in pairs.

The asymptotical directions are determined by:

$$(q^2-s)(x^2-y^2)^2+4q(q-s)x^2y^2=0.$$

They are real if q^2-s and $q(q-s)$ have different signs.

They coincide in pairs:

for $s=q^2$ $(r=0)$ with the directions of the axes,

for $s=q\left(r=\frac{1}{4}(1-q)\right)$ with the directions of the bisectrices.

For $s=q^2$ the asymptotes are removed at a distance $\sqrt{\frac{1}{1-q}}$ from O, for $s=q$ at a distance $\frac{1}{2}\sqrt{\frac{-2q}{1-q}}$.

For $s=q^2$ (L') touches (C) in 4 points, lying on the axes, for $s=q$ in 4 points on the bisectrices (§ 5).

If the points of inflexion coincide in pairs those points are situated either on the axes or on the bisectrices.

If they are lying on the axes at a distance a from O, then the equation should run:

$$(x^2+y^2-a^2)^2 = s'(x^2-a^2)(y^2-a^2).$$

From this we deduce:

$$s=\frac{q^2}{(1-2q)^2}\,;\ \left(r=q^2\frac{(1-q)}{(1-2q)^2}\right)\,;\ a^2=\frac{2q-1}{q-1}.$$

The points of inflexion coincide in pairs on the bisectrices for:

$$s=\frac{q^2}{(q-2)^2}\ ;\ \left(r=\frac{q(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2}\right)\ ;\ a^2=\frac{2-q}{1-q}.$$

From what was observed in § 7 follows that we have to consider for q negative values only, and positive ones smaller than unity.

The asymptotes, parallel to the axes, are real for all these values of q.

The asymptotes, parallel to the bisectrices, are real for negative values of q, imaginary for positive ones, smaller than unity.

The points where the points of inflexion coincide on the bisectrices, are always real.

The points where the points of inflexion coincide on the axes are real for all negative values of q, and further for positive values of q, smaller than $\frac{1}{2}$. For values of q between $\frac{1}{2}$ and 1 they are imaginary. Further we observe that the value of s, for which these points occur, is between ∞ and q, if q lies between $\frac{1}{4}$ and $\frac{1}{2}$; s lies between q and q^2, if q lies between 0 and $\frac{1}{4}$.

After the deductions made in § 6 and § 7 and this § it will be superfluous to give an explanation of fig. 7, where (L') is represented for a negative value of q and some various values of s, and fig. 8, where (L') is represented for a positive value of $q\left(<\frac{1}{4}\right)$.

§ 11. From the shape of (L') that of (L) as reciprocal polar curve may be at once deduced.

Let in the first place q be negative. There are 4 pairs of parallel asymptotes, touching at the circle $x^2+y^2=\frac{1}{2}$. They are parallel with the bitangents of (L'), passing through O. Let us now consider various values of s.

$s>q^2$. $(r<0)$. Fig. 9. Besides the 8 asymptotes just mentioned there are 4 more, which pass through O. The entire curve (L) lies outside (C) and can therefore not be of any consequence as an envelope. For on (C) the velocity of the moving point is 0; outside (C) the vis viva would be negative. In fact q^2 is the greatest value that s can have in the dynamical problem.

$s=q^2$. $(r=0)$. Fig. 10. The cusps have coincided in pairs in the axes, with which the four asymptotes passing through O have now coincided in pairs. (L) touches in 4 points at (C).

The only forms of motion which the dynamical problem allows of are an X-vibration, and a Y-vibration.

$\frac{q^2}{(1-2q)^2} < s < q^2 \left(q^2 \frac{(1-q)}{(1-2q)^2} > r > 0 \right)$. Fig. 11. (L) delimits two quadrilateral domains of motion with vertices on (C) [1].

$s = \frac{q^2}{(1-2q)^2} \cdot \left(r = q^2 \frac{(1-q)}{(1-2q)^2} \right)$. On the axes 4 pairs of cusps have coincided. (L) deviates only a little from the shape indicated in Fig. 11.

$0 < s < \frac{q^2}{(1-2q)^2} \cdot \left(-\frac{1}{4} q > r > q^2 \frac{(1-q)}{(1-2q)^2} \right)$. Fig. 12.[2] 8 cusps occur. (The "stirrups" lying within the domains of motion contribute indeed to the envelope).

$s = 0 \left(r = -\frac{1}{4} q \right)$. Fig. 13. Degeneration in 8 asymptotes.

Two domains of motion each bounded by a square.

We now get to the negative values of s. No figures have been drawn for them as they are of exactly the same nature as those for the positive values of s; we have only to revolve the figures 45°. Consequently:

$\frac{q^3}{(q-2)^2} < s < 0. \left(\frac{q\,(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2} > r > -\frac{1}{4}q \right)$. Fig. 12, having revolved 45°.

$s = \frac{q^3}{(q-2)^2} \cdot \left(r = \frac{q\,(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2} \right)$. Here we have to take into consideration that the distance of the special points to O is another one than for

$$s = \frac{q^2}{(1-2q)^2}.$$

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[1] One domain of motion is bounded by two opposite branches a, as far as they are lying inside (C), and the branches b which pass through the points of intersection of the just mentioned branches a with (C).

[2] This Fig. and Fig. 18 we also find in a treatise of F. KLEIN: "Uber den Verlauf der ABEL'schen Integrale bei den Curven vierten Grades". (Math. Ann. 10. Bd, 1876).

$q < s < \frac{q^3}{(q-2)^2} \cdot \left(\frac{1}{4}(1-q) > r > \frac{q(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2}\right)$. Fig. 11, having revolved 45°.

$s = q \cdot \left(r = \frac{1}{4}(1-q)\ .\right)$. Fig. 10, having revolved 45°. The distance of the cusps to O has changed however.

$s < q \cdot \left(r > \frac{1}{4}(1-q)\right)$. Fig. 9, having revolved 45°.

Let us now suppose that q *is positive and* < 1.

$s < q \cdot \left(r > \frac{1}{4}(1-q)\right)$. Fig. 14. (L) has no dynamical meaning for the same reasons as in Fig. 9.

$s = q\left(r = \frac{1}{4}(1-q)\right)$. Fig. 15. The dynamical problem allows of two simple vibrations only.

$\frac{q^2}{(1-2q)^2} < s < q \cdot \left(q^2 \frac{(1-q)}{(1-2q)^2} < r < \frac{1}{4}(1-q)\right)$. Fig. 16. Two domains of motion. [1])

$s = \frac{q^2}{(1-2q)^2}\left(r = q^2 \frac{(1-q)}{(1-2q)^2}\right)$. The cusps of the preceding Fig. have coincided in pairs now.

$q^2 < s < \frac{q^2}{(1-2q)^2}\left(0 < r < q^2 \frac{(1-q)}{(1-2q)^2}\right)$. Fig. 16, from which the cusps have disappeared.

$s = q^2$. $(r = 0)$. Fig. 17. (L) has 4 points of contact with (C). In the dynamical problem we are concerned with an asymptotical approach to the X- or Y-vibration. This case should be considered as the transition between two domains of motion and a single domain of motion.

$\frac{q^3}{(q-1)^2} < s < q^2 \cdot \left(\frac{q(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2} < r < 0\right)$. Fig. 18. The "stirrups" contribute to the "envelope". [2])

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[1]) Of the closed branch of (L) 4 parts lie inside (C). Each of the domains of motion is bounded by 2 opposite parts and by the infinite branches that pass through their final points.

[2]) The inner branch serves partly as exterior, partly as interior envelope. The parts which, seen from the centre, are hollow, touch internally, the rest externally.

$s=\frac{q^3}{(q-2)^2}\cdot\left(r=\frac{q(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2}\right)$. The cusps of Fig. 18 have coincided in pairs.

$0<s<\frac{q^3}{(q-2)^2}\cdot\left(-\frac{1}{4}q<r<\frac{q(q-1)\left(1-\frac{1}{4}q\right)}{(q-2)^2}\right)$. Fig. 19 ¹)

$s=0.\ \left(r=-\frac{1}{4}q\right)$ Fig. 20. Degeneration in the circle $x^2+y^2=\frac{1}{2}$.

We have now supposed, that q lies between 0 and $\frac{1}{4}$. If q lies between $\frac{1}{4}$ and $\frac{1}{2}$, we have a little change. Then the 8 cusps of Fig. 14 would already have disappeared for $s=q$.

For q between $\frac{1}{2}$ and 2 the forms of the envelope, indicated by Fig 16, do not exist.

For q *positive and* >1 no figures have been drawn for reasons stated already.

§ 12. Let us now consider the shape of (L) in general, first in case (K) is an ellipsis.

The symmetry with regard to the axes and the bisectrices does not exist anymore now. The nodes, which for $l=0$ lie on the axes, lie for positive values of l in the second and the fourth quadrant (§ 3); those which lie for $p+q=0$ on the bisectrices have been removed for positive values of $\frac{p+q}{p}$ into the direction of the Y-axis (§ 3). The changes in form which (L) undergoes in consequence of this are easily understood.

Other forms of (L) are, however, possible.

Let us first suppose $p>0$. We have to start now from the 5 cases mentioned in § 6.

In case 1, (L) has mainly the shape which has been represented in Fig. 9, in which we have to take into consideration the observations just mentioned.

In case 5, (L) has, with due observation of these remarks, the general shape of Fig. 11, or of Fig. 12, or it is a combination of

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¹) For $q=1$ (S) consists of two circles; we have then the well known case of the conical pendulum.

those two forms, i.e., the envelope of one system of osculating ellipses has 4 cusps, the envelope of the other has none.

Case 2 is to be considered as a combination of Fig. 9 and Fig. 10. a touches (C) in two points, b has two cusps on the line which connects O with the points of contact of a with (C). The dynamical problem allows of a single simple vibration.

Case 3 gives rise to a combination of Fig. 10 and Fig. 11 (or Fig. 12). There is *one* system of osculating ellipses.

Case 4 to a combination of Fig. 10 and Fig. 11 (or Fig. 12). There is *one* system of osculating ellipses. Moreover the dynamical problem allows of a simple vibration.

In the case $p < 0$ we have again in the first place envelopes corresponding in the main with those represented in the Fig. 14—20. We should, however, bear in mind, that in general the cusps do not disappear by 8 but by 4 at a time. There is for instance a transitional form possible between Fig. 18 and Fig. 19 in which 4 cusps occur, and in Fig. 14 and Fig. 15 4 cusps may have fallen out. In order to obtain the other forms of the envelope we must make use of the observation about (L') in § 7.

If the branch of (L) lying outside (C) touches (C) in two points, then the dynamical problem allows of *one* simple vibration. If (L) cuts (C) in 4 points, then we get one of the two domains of motion of Fig. 16, etc.

Is (K) an hyperbola or a degeneration then the various shapes of (L) may be deduced in the same way from the Fig. 3—6.

Physiology. — *"On the reflectorical influence of the thoracal autonomical nervous system on the rigor mortis in cold-blooded animals."* [1]). By S. DE BOER. (Communicated by Prof. C. A. PEKELHARING.)

(Communicated in the meeting of January 31, 1914).

The rigor mortis that is caused by hardening and shortening of the muscles begins in warm- and cold-blooded animals after the circulation of the blood has stopped for some time, in warm-blooded ones 5—8 hours, in cold-blooded ones 1—2 days. If with a muscle that has been removed, we make provision for a sufficient supply of oxygen, it mortifies without stiffening. A special chemical state

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[1]) According to experiments made in the physiological laboratory of the University of Amsterdam.

that is caused by a deficiency of oxygen, is consequently an indispensable condition for rigor mortis of the muscles, HERMANN showed moreover that the process of rigor mortis is accelerated from the central nervous system, whereas EWALD ascribed this accelerating influence to the labyrinth.

Last year I established, that, both for warm- and cold-blooded animals, the tonus of the skeleton-muscles is entertained by impulses reaching the muscles along the efferent, thoracal autonomical nerve-tracks [1]). I demonstrated this by the section of the Rami communicantes on one side, after which the muscles of the same side become atonic. In this way I could fully ascertain, by a physiological experiment, the double innervation established by BOEKE [2]) on account of morphological investigations, and, at the same time, I could establish the signification, which autonomic innervation has on the transversally striped muscles.

In the many operations that I made on frogs, I was struck by the fact that, after death, the hind-leg of the operated side was still supple, when the other hind-leg was already quite stiff. So on January the 13th I cut the right Rami communicantis and the sympathetic chain of a frog as high as possible. The next afternoon at 6 o'clock the frog was no longer very active. On the 15th of January I found it dead, all limbs were supple. Now I laid down the frog with both hind-legs flexed in the same way. At 4 o'clock of the afternoon the right fore- and hind-legs are still quite supple. The left hind-leg however is, both in hip- and knee-joint, stiff in flexed position with strengthened dorsalflexion in the foot-joint. The left shoulder- and elbow-joint are also stiffened. The axis of the body is flexed with the concave side to the left. These particulars can easily be observed in the photograph.

At half past five the condition is still unchanged.

At half past eight p. m. there is likewise a beginning of rigor mortis in the right hind-leg and in the right shoulder. At eleven o'clock the right fore- and hind-legs are also quite stiffened. On the 18th of January the rigor mortis has entirely ceased. This observation was made at a temperature of 17° Celsius. Consequently the rigor mortis began, on the side where the Rami communicantes had been cut, 7 hours later than on the other side, where the muscles were still connected with the spinalcord by means of the autonomic nerve-tracks. This observation induced me to a series of intentionally

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[1]) Folio Neurobiologica VII (1913) 378 and 837.

[2]) Verslag der Wis.- en Natuurk. Afd. Kon. Akad. v. Wetensch. Amsterdam, April 1909. Deel XVII, p. 1008—1012.

Frog of which the right Rr. communicantes have been cut through in the beginning stage of rigor mortis. The left shoulder and elbow are stiffened, the left hind-leg is stiffened in flexed position both in hip- and knee-joint with strengthened dorsal-flexion of the foot. The axis of the body is bent with the concavity to the left.

The right fore- and hind-legs are still quite supple.

made experiments in which I removed, as much as possible, incalculable influences. I proceeded in the following manner:

A short time before I hung the frog in the damp case, or occasionally a few days previously, I cut, on the right side, the Rami communicantes and the right sympathetic chain at the top. By binding up the heart I killed the frog, then I passed a thread through the two jaws, and on these I hung the frog in a closed, glass-case that was kept damp by a wet sponge and by thoroughly wet filter-paper on the bottom. The damp case was then placed in a room in which the temperature was raised as high as 30° to 35° Celsius. The frog was consequently placed in regularly heated damp surroundings. By this higher temperature the process of rigor mortis is considerably shortened. It could easily be observed in these frogs, that the right hind-leg hung down suppler than the left one, that consequently the tonus had disappeared from the muscles at the right side.

A short extract from the protocols may follow here:

I. *17 January.* All Rami communicantes of the right side are cut.

20 January: After the heart has been bound up the frog is hung in the damp case.

4.30. Left hind-leg is drawn up, stiffness in hip, knee-joint and foot. The left elbow-joint is stiffened, no difference is to be observed in the two shoulder-joints.

Right elbow and whole right hind-leg are still supple.

5.30. Situation still the same.

9.30. The two hind-legs are hanging in stiffened tense and abduction position; the two fore-legs stiffened in flexed position.

22 January. Rigor mortis has ceased.

II. *21 January.* 1.15. The Rr. communicantes are cut through.

1.30. The heart is bound up. The frog is hung in the case.

5.30. Left shoulder-joint is stiff, other joints are still supple.

7.30. Situation unchanged.

8.30. Beginning of rigor mortis of the left hip.

9. Right shoulder begins to become stiff.

10. Left elbow stiffened.

11.30. Left knee begins to stiffen, the hip is quite stiff.

22 January. Stiffened tense and abduction position in all joints of the hind-legs.

23 January. 9 a. m. The rigor mortis has ceased.

III. *19 January.* 11.15 a. m. The Rr. communicantes are cut through.

11.30. The frog is hung in the case after the heart has been bound up.

4. p. m. Left fore-leg stiffened in the elbow- and shoulder-joints, left hind-leg is strongly flexed and stiffened in the hip, dorsal flexion and rigor mortis of the foot-joint.

4.30. Left knee is becoming stiff.

5. p. m. Right elbow-joint, knee and hip begin to become stiff.

6. p. m. Entire rigor mortis with abduced and tense hind-legs and expanded webs.

24 January. 12 a. m. The rigor mortis has ceased.

IV. *22 January*. 11.15. The Rr. communicantes are cut through.

11.30. The frog is hung in the case after the heart has been bound up.

5. p. m. Beginning of rigor mortis in left elbow and shoulder.

9.30 p. m. Left fore-leg entirely stiffened, right one only in the shoulder-joint. Left hip and knee entirely stiffened in flexed position. Beginning of rigor mortis of right hip, right knee-joint is still supple. Right foot is still supple, whilst the left one is entirely stiffened. The entire left hind-leg hangs with strong flexion in the hip tense foot and expanded webs. The right hind-leg hangs still in the usual slightly flexed position.

10.15. Situation unchanged.

11.30. The left hind-leg shows stiffened tense position, the right hip-joint entirely stiffened, beginning of rigor mortis in the right knee and foot. Temp. is 28° Celsius.

23 January 9 a. m. Both hind-legs are hanging in completely stiffened tense and abduction position.

24 January. The rigor mortis has ceased.

V. *23 January*. 8.45 a. m. The Rr. communicantes are cut through.

9 a. m. The frog is hung in the damp case after the heart has been bound up.

1 p. m. Left shoulder and hip show more resistance than right ones. Left hind-leg drawn up with strong dorsal flexion of the foot.

2 p. m. In left knee and foot more resistance than in right ones.

3 p. m. The right hip becomes also stiffer.

4 p. m. The two hind-legs are hanging in tense and abduction position.

VI. *24 January*. 8.45 a. m. The Rr. communicantes are cut through.

9 a. m. The frog is hung in the damp case.

12. Beginning of rigor mortis of left shoulder-joint.

4 p. m. Left hip shows more resistance than right one.

4 30. Left hind-leg stiffened, with strongly flexed hip, knee and foot

6 p. m. Left hind-leg still in stiffened flexed position. The right one is still quite supple. Both the shoulder-joints are stiffened.

8.30. Beginning of rigor mortis in the right hip.

9.30. Right hip entirely stiff, the knee is still supple.

10.30. Right knee also entirely stiffened, the right foot is still supple.

26 January. 10 a. m. Both hind-legs are hanging in stiffened tense and abduction position.

26 January 5 p. m. The rigor mortis has ceased.

VII. *24 January*. 9.15. The Rr. communicantes are cut through.

10 a. m. Frog hung in the case after the heart has been bound up.

5.30. Left hind-leg more flexed in the hip and with greater dorsal flexion of the foot than right one.

6.30. When lifting the left hind-leg greater resistance than in the right one.

9.30. Stronger resistance in the left hip.

10.30. Left hip, knee and foot are stiff in flexed position, right hip beginning of rigor mortis; right knee and foot still quite supple.

26 January. Both hind-legs are hanging in stiffened extension- and abduction-position (25 Jan. not controlled).

26 January. 5 p.m. Rigor mortis has ceased.

VIII. *26 January.* 9.45. The Rr. communicantes are cut through.

10 a. m. Frog hung in the damp case, after the heart has been bound up.

1 p. m. All joints still supple.

6 p. m. Left shoulder and elbow stiffened, slight rigor mortis in left hip.

9 p. m. Left hind-leg completely stiffened in tense position with expanded webs.

Right shoulder and elbow also stiff, but less so than left ones. Right hip stiff in flexed-position, but right knee and foot are still supple.

So I have made a series of 20 experiments in which I always found retardation of rigor mortis on that side where I had cut through the Rr. communicantes. The process of rigor mortis is consequently accelerated, when the muscles are connected with the central nervous system by means of the efferent autonomic nerve-tracks. In the first operation, which was performed at roomtemperature the operated side stiffened at least 7 hours after the not operated one. But also in experiments that I made at a temperature of over 30° Celsius, the difference was even 1 or 2 hours. The experiments mentioned here were made on individuals of Rana esculenta. I made also some experiments on Rana temporaria, in which the process of rigor mortis went off quicker. In my opinion the reason of this is to be found in the much thinner limbs by which the relation between volume and surface of the muscles becomes less favourable. Hereby the mortification-process and the process of rigor mortis is evidently promoted. The same difference between the operated and the not operated side I observed here likewise. In all my experiments it struck me immediately that of the fore-legs the shoulder, and of the hind-legs the hip stiffens first. The knee however was now stiff before the foot, now the reverse took place. With slight deviations this occurred thus according to the law of NYSTEN.

Further in all my experiments the flexors stiffened first and afterwards the tensors. No exception was made in this respect for the hind-legs, so that at the end of each experiment the hind-legs were in a tense position. Further I must point out that in all my experiments the rigor mortis was accompanied by a shortening of the muscles, first rigor mortis and shortening of the flexors, then of the tensors.

HERMANN, who first proved that the process of rigor mortis was accelerated under the influence of the central nervous system, took rigor mortis for a last contraction of the muscles. Because, as I have just shown, rigor mortis is influenced by the central nervous system along the autonomic nerve tracks, as is likewise the case with the muscle-tonus, I am of opinion that rigor mortis is a last tonical muscle-shortening. This view is also entirely in keeping with PEKELHARING'S [1] investigations, who proved that the percentage of creatine of the muscles increases with rigor mortis, as is likewise the case with increased tonus.

Now the question arises: how is rigor mortis brought about? The usual explanation is, that through the mortification of the central nervous system the muscles receive stimulants along the nerve-tracks, and these stimulants accelerate rigor mortis. EWALD was of opinion that these stimulants originate in the labyrinth, whilst FLETCHER proved that supply of oxygen makes the muscles mortify without rigor mortis. I think I can now give a more general explanation, corresponding with the facts that are known.

We know that rigor mortis only begins, when the circulation of the blood has ceased. We obtain then in all tissues an accumulation of products of metabolism consequently suffocation. And now it is known that, if we kill an animal by hemorrhage or suffocate it by pinching off the trachea, that then, by the influence of the autonomic nervous system, the body shows manifold irritation-situations: through tension of the arrectores pilorum the hairs stand erect in the dorsal skin-regions of the trunk and in the tail; the bladder empties itself and also the rectum. In an entirely analogous way the sending of more powerful stimulants of the tonus to the skeleton-muscles takes place. The stimulants running centrifugally, which during life-time entertain the muscle-tonus by means of the thoracal autonomic nervous system, will now, at this increased irritability, after death cause a last powerful tonical shortening of the muscles.

When I had established in this way, that the occurrence of rigor mortis stands under the influence of the thoracal autonomic nervous system the question rose, if, at least in frogs, this influence, just like the tonus, as P. Q. BRONDGEEST [2] has proved, is entertained by stimulants produced along the posterior roots of the spinal cord.

In this direction I made already 10 experiments. I cut the posterior-roots 8, 9, and 10 of a frog at one side. From the doctrine of segmental anatomy we know, that these posterior roots contain the sensitive nerve-tracts of the hind-leg.

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[1] Onderzoekingen van het Physiologisch Laboratorium te Utrecht 5de R. XI pag. 1. 1910.

[2] P. Q. BRONDGEEST, Over den tonus der willekeurige spieren. Diss. Utrecht 1860.

Only such frogs as could still leap well after the operation, and in which from the leg at the operated side no reflexes could be excited, whilst it could be done at the other side, and that showed the so-called "Hebephaenomenon" of HERING were used for my experiments. I add here a few protocols:

I*a*. *6 February*. Rana esculenta, of which posterior root 8, 9, and 10 of the left side are cut. The frog continues leaping after the operation and makes good use of the two hind-legs. The left hind-leg shows after the leap a new elevation of the foot as HERING has observed. Reflexes at the left hind-leg have ceased, a crossed reflex-movement through strong irritation of the right hind-foot is observed. The reflexes at the right side are lively.

7 February 9.30. The frog which is in a very good condition is hung at 30° Cels. in the damp case after the heart has been bound up.

12.30. The right hind-leg shows increased dorsal flexion in the foot-joint.

1.30. The dorsal flexion of the right leg has increased; when lifting the hind-legs a stronger resistance on the right side than on the left one, likewise in the knee and the hip. Left hind-leg still supple. Both fore-legs are likewise still supple.

2.30. Still the same situation as 1.30.

3.30. In right hind-leg still more resistance, left hind-leg still quite supple.

4 p.m. Right hind-leg is in stiffened tense and abduction position with expanded webs, foot-joint still supple.

5.30. The right hind-leg is quite stiffened in knee and hip, in the foot-joint partial rigor mortis. The left hind-leg is supple in all joints. On both sides there is rigor mortis in shoulder and elbow.

8 February 10 a.m. The frog has been hanging from 5.30 last night in the damp case at 15° Cels.

The right foot is now likewise stiffened, so that the right hind-leg stands in entire tense and abduction position with expanded webs. The left hip is entirely stiffened, left knee and foot-joint are still movable.

9 February 10 a.m. The left leg is now also stiffened, only the knee is still somewhat, but very little, less stiff than the right one.

II*a*. *10 February*. Little Rana esculenta, of which on the 9th of Febr. posterior roots 8, 9, and 10 have been cut, on the leftside. Mobility and reflexes as with the former frog.

10 a.m. The heart is bound up. The animal is placed in the damp case at 30° Cels. for the experiment.

1.30 p.m. The dorsal flexion of the right foot has increased, likewise the hip flexion on the right side. Right hip begins to be stiffened, left hind-leg is still quite supple.

2 p.m. On the right side increase of the phenomena, on the left side still supple.

2.30. Right hind-leg almost quite stiff in still slightly flexed position, left hind-leg still supple.

3,30. Right hind-leg in stiffened tense and abduction position, the left one is stiff in the hip; knee- and foot-joint of the left leg still supple.

4.30. Both hind-legs are hanging in stiffened tense- and abductionposition with expanded webs.

IIIa Very large Esculent.

10 Febr. 10.45. The right posterior roots 8, 9, and 10 are cut.

11 p.m. After the heart has been bound up, the frog is placed in the damp case at 30° Cels.

3.30 p.m. Rigor mortis in the left hip.

4.30. Left hind-foot is entirely stiffened, only the foot is still a little movable. The right hind-leg is still quite supple. Both fore-legs are stiff. Now I remove the case with the frog to a surrounding of 17.5° Cels.

11 Febr. 10 a.m. Right hind-leg is now likewise entirely stiffened, only the foot is still partly supple.

11 Febr. 5 p.m. The right hind-leg is still somewhat supple in the foot-joint.

12 Febr. Both hind-legs stiffened in all joints.

IVa. *10 Febr.* The left dorsal roots 8, 9 and 10 of large Esculent are cut.

11 Febr. 9.30. Hung in damp case at 30° Cels.

11.30. Right hind-leg with expanded webs, when lifting it the right leg shows increased resistance. Left hind-leg still quite supple.

1 p.m. Right hip rather stiff, left one still quite supple.

3 p.m. Right hip rather stiff, right knee drawn up. Left hind-leg still quite supple.

5 p.m. Right hip entirely, knee- and foot-joint partly stiff, much increased flexion position to the right. Left hind-leg still quite supple, the webs are here expanded.

5.30. Right hind-leg stiff in flexion-position, only the foot-joint is partly stiff; left hind-leg is still supple in all joints. Both fore-legs stiffened. Frog is now placed in a surrounding of 15° Cels.

12 Febr. 9 a.m. Situation still exactly the same as last night at 5.30. From this moment temperature at 30° Cels.

12 at noon. Left hind-leg begins to become stiff in knee and hip; right foot-joint still partly stiff.

1.30 p.m. Right hind-leg also stiffened in the foot-joint, entire tense-position; left hind-leg in tense position stiff in knee and hip, left foot is still partly supple.

Va. *12 Febr.* 9.45 a.m. Right dorsal root 8, 9, and 10 cut through.

10 p.m. The frog is hung in the damp case at 30° Cels.

1 p.m. The left leg begins to draw up, the flexion in the hip and the dorsal flexion of the foot increase.

2 p.m. Left hip strongly flexed; left foot strongly dorsally flexed, on the left side increased resistance when lifting. Right leg still supple.

4 p.m. Left hip entirely stiff, knee and foot begin to be stiffened. Right hind-leg begins to draw up.

6 p.m. Right hip and knee now likewise partly stiff, foot is still supple. Left hind-leg in tense position with still partly supple foot, right hind-leg in flexion-position.

13 Febr. 10 a.m. Both legs are hanging in stiffened tense- and abduction-position with expanded webs.

From these experiments, which I intend to continue it appears clearly, that the cutting of the appurtenant dorsal roots causes retardation of the rigor mortis of the muscles.

In this way we have proved that the view of HERMANN is incorrect, according to which the influence of the central nervous system on the occurrence of rigor mortis should be caused by the mortification of the higher centra by which impulses should be driven towards the muscles. For in my experiments in which I cut on one side the posterior roots, the way from the central nervous system to the muscle is nowhere interrupted; only the supply of reflexstimulants (from the proprioceptores) is prevented. Rigor mortis is consequently also caused by a reflectoric process.

If we ask now how we are to understand the tonical innervation for accelerating rigor mortis, the answer must run, in my opinion, pretty well as follows.

We know from FLETCHER and WINTERSTEIN that the indispensable cause of rigor mortis is to be found in a chemical state of the muscles, which is caused by want of oxygen.

This "chemical state" will certainly depend on the existence of products of metabolism. It is for the present unknown which are these products. There are however, I surmise, sufficient reasons to admit that they are products of partial transmutation, for supply of oxygen, which certainly encourages transmutation, prevents rigor mortis, and increase of temperature which also promotes transmutation, accelerates rigor mortis.

We can reconcile these two facts in no other way than by admitting that in the first case the ample supply of oxygen causes the processes of metabolism to take their normal courses to the end, consequently to complete oxydations, during which then the obnoxious intermediate products do not come into existence, or do not continue to exist. In this way it is also comprehensible that increase of temperature promotes rigor mortis so much,because with the metabolism, taking place then with still greater rapidity and intensity, the want of oxygen, resp. the deficit of oxygen, is felt so much the stronger.

If now in this respect we compare the two hindlegs of a frog of which on one side the reflex-stimulants for the tonus have no longer access, then the leg with intact reflex-track has muscles that are in a state of tonus, whilst the tonus in the other side has disappeared. The leg with muscles in tonus, requiring for the entertainment of this situation more metabolism will consequently show a more rapid and intensive accumulation of intermediate products of metabolism than the atonic leg, which does notrequire so much oxygen on account of less intensive metabolism.

Consequently the muscles that are in a state of tonus satisfy better the indispensable condition of rigor mortis, namely suffocation, than the atonic ones. The leg with tonus muscles also satisfies better the 2nd condition namely the condition of being influenced by the nerves.

For these muscles constantly receive indeed stimulants by way of reflection, whereas the other atonic leg remains without these stimulants. The consequence of both the more intense alteration of the chemical state and the influence of the reflection is that the leg of which the tonus-reflection track remains uninjured, stiffens sooner than the leg of which this reflection-track is interrupted at the posterior roots or near the Rami communicantes. We must thus consider the rigor mortis of the skeleton muscles as a last vital demonstration of the muscles under the influence of suffocation, whilst stimulants running along the tonus-reflection-track accelerate this process. That rigor mortis is a last (tonical) contraction of the muscles is apparent from the fact that the muscles that have lost their irritability in an atmosphere of oxygen, can no more stiffen or shorten under circumstances of suffocation.

Chemistry. — *"On the reduction of aromatic ketones"*. II. By Prof. J. Böeseken and W. D. Cohen. (Communicated by Prof. A. F. Holleman).

(Communicated in the Meeting of February 28, 1914).

In our previous communication on this subject [1]) we have assumed that by reduction of the ketones the half pinacone molecule is in all cases the sole direct reduction product.

If, in the position where that partial molecule is formed, there are practically no OH-ions it polymerises immediately to pinacone.

In the presence of OH′, however, there was always found benzhydrole and the question arose whether this was caused by direct reduction or by the transformation of the previously formed pinacone into benzophenone and benzhydrole by the OH-ions.

These alternatives may be represented by the schemes

$$(C_6H_5)_2CO \rightarrow (C_6H_5)_2COH \rightarrow (C_6H_5)_2CHOH \quad . \quad . \quad . \quad (I)$$

$$(C_6H_5)_2CO \rightarrow (C_6H_5)_2COH \rightarrow [(C_6H_5)_2COH]_2 \rightarrow (C_6H_5)_2CHOH + \\ + (C_6H_5)_2CO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

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[1]) Proc. XVI, 91 (1913).

If the latter is the case, the pinacones belonging to the ketones which, in a neutral or very faintly alkaline medium, give much hydrole must be decomposed by alkalis into a mixture of hydrole and ketone much more rapidly than those which in the same circumstances yield but little hydrole.

It may even be expected that the formation of hydrole and the splitting of the pinacone by alkalis will proceed in a strongly parallel manner.

This has now indeed proved to be the case. The greater the decomposition velocity of the pinacone by alkalis, the smaller the quantities formed in the reduction with aluminium amalgam.

With this is also proved that at the boundary layer of the amalgam is present an excess of OH-ions which is only accessible to the pinacone in its nascent state. If, for instance, pinacone is exposed to the action of aluminium amalgam and 80°/₀ alcohol, it is practically not attacked, moreover the proportion in which pinacone and hydrole are formed is nearly independent of the duration of the reduction. (1st communication p. 92).

The proportion of the quantities of pinacone and benzhydrole in which these are formed during the reduction of thirteen aromatic ketones with aluminium amalgam has been given in the 1st communication p. 98.

The decomposition velocity of the pinacones was determined by dissolving quantities of 0.5 gram in a mixture of 75 cc. of ether and 5 cc. of alcohol diluting this solution to 105 cc. with alcoholic solutions of potassium hydroxide of $N/0.42$, $N/0.042$ and $N/0.0042$ strength, respectively. The normalities of the solution thus become 0.1, 0.01, and 0.001.

These mixtures were kept for definite periods at 25°, then diluted with cold water, agitated a few times with ether, the ethereal solution was evaporated down rapidly and the residue digested with 80°/₀ alcohol at 25° in the manner described previously (l. c. p. 9) in order to get to know the quantities of undecomposed pinacone.

The subjoined table and graphic representations give a survey of the results obtained.

The numbers of the lines in the graphic representations appertain to the numbers with which the pinacones are indicated in the table; the percentages next to or below those numbers in the graphic representation indicate the quantities of pinacone formed from the respective ketones by reduction with aluminum amalgam in 80°/₀ alcohol.

From the graphic representation of the pinacone decomposition, where, as observed above, are indicated the percentages of pinacone which are formed in the reduction with aluminium amalgam, it follows that these two phenomena proceed indeed in a completely parallel manner.

Pinacone.	$NaOC_2H_5$ approximate concentration.	Time of action in minutes.	Undecomposed pinacone in mgr.
1) pinacone from benzophenone	0.1	120	0
"	0.01	15	370
"	0.01	30	270
"	0.01	60	60
"	0.001	15	500
"	0.001	30	498
"	0.001	60	488
2) pinacone from 2.chlorobenzophen	0.1	120	0
"	0.01	15	0
"	0.01	30	0
"	0.001	15	280
"	0.001	20	210
"	0.001	30	90
3) pinacone from 3.chlorobenzophen	0.001	15	0
"	0.001	25	0
4) pinacone from 4.chlorobenzophen	0.01	10	280
"	0.01	15	200
"	0.01	23	80
"	0.01	30	0
"	0.001	30	430
"	0.001	60	370
5) pinacone from 4.bromobenzophen	0.01	10	270
"	0.01	15	190
"	0.01	30	0
"	0.001	30	440
"	0.001	60	380
6) pinacone from 44′chlorobenzophen	0.01	10	0
"	0.01	15	0
"	0.001	10	300
"	0.001	15	200
"	0.001	25	0
7) pinacone fr. 4 methoxybenzophen	0.01	15	440
"	0.01	30	390
"	0.01	60	270
"	0.001	30	not attacked
"	0.001	60	
8) pinacone from 4 methylbenzophen	0.01	15	480
"	0.01	30	450
"	0.01	60	370
"	0.001	15	not attacked
"	0.001	30	
"	0.001	60	
9) pinacone fr. 44′ dimethylbenzoph.	0.01	30	475
"	0.01	60	450
"	0.01	90	430
"	0.001	60	not attacked
"	0.001	120	
"	0.1	90	0
10) pinacone fr.2′Cl 4 methylbenzoph.	0.01	10	260
"	0.01	15	180
"	0.01	30	0
"	0.001	30	430
"	0.001	60	370
11) pinacone fr.4′Cl4 methylbenzoph.	0.001	15	0
"	0.001	25	0

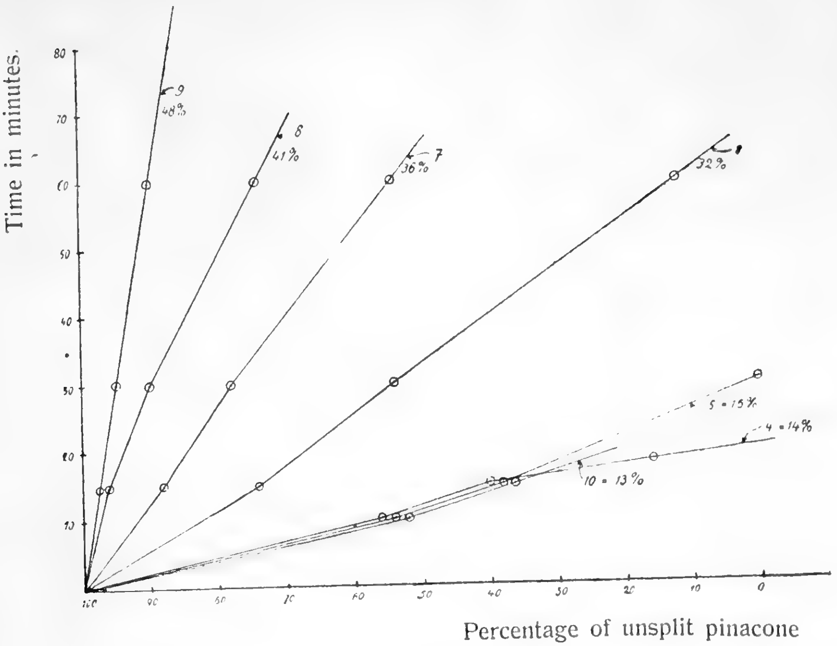


Fig. 1.

Decomposition of the pinacones in 0.01 *n* $NaOC_2H_5$.

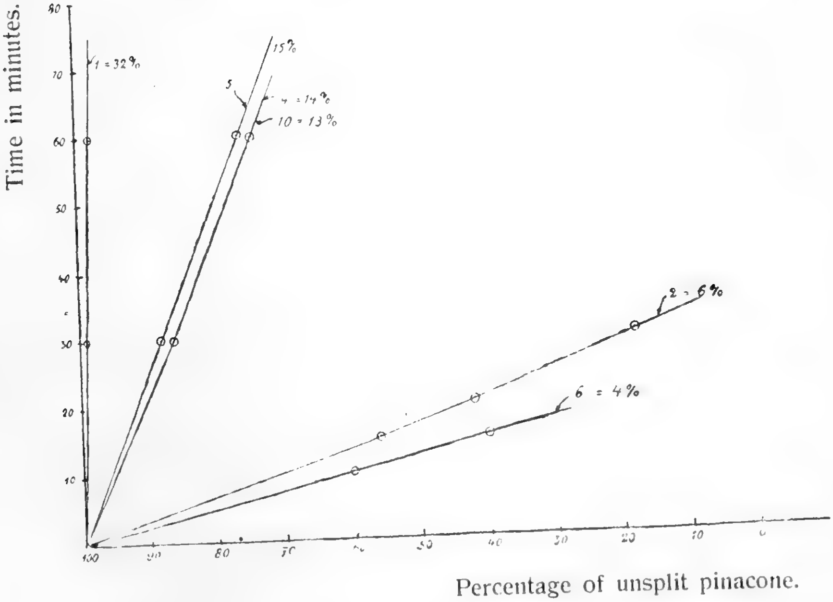


Fig. 2.

Decomposition of the pinacones in 0.001 *n* $NaOC_2H_5$.

One gets the impression that in the reduction of benzophenone and its derivatives, the oxygen only is attacked and that on gentle reduction there takes place an exclusive addition of a hydrogen atom to the oxygen. Whatever happens afterwards has nothing more to do with that reduction.

If there are no OH-ions, pinacone [1]) is formed, but if these are present a splitting into hydrole and ketone takes place and the latter can be again attacked by the hydrogen. If the hydroxyl-ions are exclusively present in the boundary layer, we shall obtain a definite proportion of pinacone and hydrole; if they are found also in the solution in a sufficient concentration all the ketone is converted into hydrole.

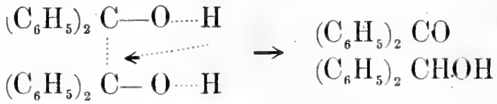
In the case of a very violent reduction, for instance, with zinc amalgam and strong hydrochloric acid [2]) the oxygen seems also to be attacked by preference and becomes apparently completely detached; the residual molecular part now, however, also absorbs hydrogen and is converted into hydrocarbon.

2. The progressive change of the gentle reduction is herewith explained in general traits, at least in so far purely aromatic ketones are concerned.

The hydrole formation thus depends in the first place on the facility with which pinacone gets resolved and this is in a high degree promoted by alkalis.

This action of bases, has meanwhile been much elucidated by the researches of W. Schenck, T. Weickel, and A. Thal (B. **44**, 1183 (1911) and **46**, 2840 (1913). There it was shown that pinacones form with the alkali metals compounds of the trivalent carbon, for instance $(C_6H_5)_2\,COK$; we notice that the central C—C-bond, which in the ketones is not particularly strong, becomes much looser still under the influence of these metals so that the half pinacone molecules, under the influence of the metal atom, can indeed lead a free existence.

In the comparatively faintly alkaline solutions matters will not proceed so far, but here those central carbon atoms can detach themselves from each other in consequence of an intramolecular displacement of atoms:



$$\begin{matrix}(C_6H_5)_2\,C\text{—}O\cdots H\\ \vdots\ \leftarrow\cdots\\ (C_6H_5)_2\,C\text{—}O\cdots H\end{matrix}\quad\rightarrow\quad\begin{matrix}(C_6H_5)_2\,CO\\ (C_6H_5)_2\,CHOH\end{matrix}$$

in which the mobile H-atoms will play a role.

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[1]) We have exposed a whole series of ketones in absolute alcohol to the action of light and never obtained a trace of hydrole.

[2]) E. Clemmensen, B. **46**, 1837, (1913).

Montagne[1]) found some years ago that a number of aromatic ketones are already reduced by boiling with alcoholic potassium hydroxide; it is very well possible that the strongly alkaline reaction of the medium increases the affinity of the ketone oxygen for the hydrogen of the alcohol molecules, so that also here half pinacone mols. are formed[2]) as follows:

$$2\,(C_6H_5)_2\,C{-}O\cdots + C_2H_6O = C_2H_4O + 2\,(C_6H_5)_2\,OH \text{ etc.}$$

The phase of the entire pinacone mols. is very rapidly gone through in this case.

It speaks for itself that this powerful affinity influence of the medium will also make its action felt on other bonds in the molecule, so that the entire phenylgroup may be resolved or halogen atoms become "activated" as found by Montagne, an action that ceases, or becomes less, when the entire $C = O$-group is saturated with hydrogen.

Conversely, this influence itself will be modified by the nature of the groups in the ketone and this the more so as the character of that group differs more from that of the hydrogen atoms. In fact, Montagne has found that the aminobenzophenones are absolutely not affected by strong alcoholic potassium hydroxide.

3. This influence of the substituents on the stability of the central pinacone-C—C bond in regard to alkalis can now be readily deduced from our measurements (see graphic representation *A* and *B* and table).

If we take the ordinary benzpinacone as the starting point, it appears that the methyl- (9 and 8) and the methoxylgroup (7) in the para-position render the molecule stable, on the other hand the halogen atoms will render the said bond looser and this in the order para (4), ortho (2), meta (table N°. 3). The para-placed bromine atom (5) joins the chlorine atom; also in the pinacone from 4.4′ dichlorobenzophenone (6) the bond is considerably looser than in the pinacone from 4 chlorobenzophenone.

Whereas in the pinacone from 2 Cl 4′-methylbenzophenone the two influences, as might be expected, counteract each other (10) it appears that in the pinacone from 4 Cl 4′-methylbenzophenone (11) the methylgroup unexpectedly promotes the loosening action of the chlorine atom.

The method followed by us thus indicates the way to mutually

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[1]) Montagne, Recueil **27**, 327 (1908).
Montagne and Moll van Charente, R. **31**, 298 (1912).

[2]) We may also express this as follows: the oxygen activated by the alkali metal withdraws the hydrogen from the alcohol molecules.

compare the action of different substituents in a molecule on a definite bond of that same molecule. If we choose the decomposition velocity of one of the pinacones as unit, the ratio of the velocities of the other pinacones to this unit is then the measure of the relative lability.

Thus we obtain for the decomposition in N/0.01 sodium ethoxide:

for 4.4.4′.4′. tetramethylpinacone (9) = 0.1
4.4′. dimethylpinacone (8) = 0.18
4.4′. dimethoxylpinacone (7) = 0.45
[pinacone (1) = 1.]
2.2′. diCl 4.4′. dimethyl ,, (10) = 2.5
4,4′. dibromo ,, (5) = 2.4
4.4′. dichloro ,, (4) = 2.3

Moreover, owing to the nature of the measurements we cannot attach to these figures more value than to an approximate determination.

4. With regard to the relative reduction velocity of the ketones to pinacones these experiments tell us nothing. In order to get to know something about this we must reduce the different ketones under the same conditions, preferably in such a manner that nothing but the pinacone is formed.

This now may be effected by exposing to light a solution of the ketones in *absolute* alcohol when indeed a ready transformation into pinacone and aldehyde takes place [1].

As it concerns here the activation of the C-O-bond it is to be expected that the relative extent of the influence of the substituents in the benzene nucleus will show quite a different order than in the pinacone resolution. We will refer to this in a future communication.

Labor. Org. Chem. Techn. University.

Delft, February 1914.

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[1] This was stated long ago by Ciamician and Silber; we have pointed out in our previous communication that in this neutral, or at most very faintly acid medium no transformation of pinacone into hydrole is to be expected and that, therefore, the absence of hydrole in this case is again a proof that the reaction proper does not extend further than to the half pinacone molecule.

Chemistry. — *"On a new method of preparing carboxylic anhydrides".* By A. J. van Peski. (Communicated by Prof. S. Hoogewerff).

(Communicated in the meeting of February 28, 1914).

Melsens (Ann. 52, p. 276) was the first to obtain sulphoacetic acid by the action of sulphuric anhydride or fuming sulphuric acid on acetic acid at a somewhat elevated temperature.

The same compound was prepared afterwards by Franchimont from sulphuric acid and acetic anhydride in which case the reaction takes place also at a higher temperature (Comp. Rend. 92, p. 1054 also this journal 1881 **16**). In an analogous manner Franchimont and others prepared some higher sulphoacids such as sulphopropionic and sulpho-isobutyric acid [1]). With regard to the formation of sulphoacetic acid according to the last method, it has already been suggested by Franchimont that it was preceded by the formation of acetylsulphuric acid. The correctness of this presumption was proved by Stillich by his isolation of the acetylsulphate of an organic base obtained in the acetylation of nitroamidobenzyl-p-nitraniline with acetic anhydride and sulphuric acid. (Ber. 38, p. 1241).

I have now succeeded in demonstrating that when, during the action of SO_3 on acetic acid, the temperature is kept below 0° primary acetylsulphuric acid is formed, which only at a higher temperature is transformed into sulphoacetic acid. The acetylsulphuric acid thus prepared is quite identical with that obtained by mixing acetic anhydride and sulphuric acid at a temperature below 0°.

Acetylsulphuric acid is capable of forming salts, the sodium compound being prepared by adding anhydrous sodium acetate to acetylsulphuric acid, when acetic acid is liberated. During this reaction the temperature must be kept below 0°. This sodium salt is insoluble in acetic acid and may therefore be obtained in a pure condition by collecting it on a filter and washing with, say, dry ether. If this sodium salt is heated either by itself or suspended in a liquid such as acetic acid or toluene it decomposes, as shown by a quantitative analysis, into acetic anhydride and sodium pyrosulphate according to the equation:

$$2\,CH_3COSO_4Na = (CH_3CO)_2O + Na_2S_2O_7$$

If, however, the sodium salt is heated with sodium acetate in presence of acetic acid, double the amount of acetic anhydride is formed:

$$CH_3COSO_4Na + CH_3COONa = (CH_3CO)_2O + Na_2SO_4.$$

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[1]) Moll v. Charante Rec. XXIV.

The anhydride formed can be obtained by distillation, sodium pyrosulphate being left behind in the first case and sodium sulphate in the second case. The so obtained sodium pyrosulphate is very voluminous and on distillation with acetic acid and sodium acetate it again produces acetic anhydride. In this case refrigeration is not necessary when adding together the three components. If, however, the above pyrosulphate is first submitted to fusion a considerable decrease in volume takes place and it is then no longer capable of forming acetic anhydride, resembling in this respect a pyrosulphate prepared in the usual manner.

In the action of sodium chloride on acetylsulphuric acid acetyl chloride is formed. In a manner analogous to that of the preparation of acetylsulphuric acid from acetic acid and SO_3, were prepared butyrylsulphuric acid and benzoylsulphuric acid, from which were obtained in a corresponding manner butyric- and benzoic anhydride, respectively.

Chemistry. — *"Connexion between the adsorption-isotherm and the laws of* PROUST *and* HENRY." By Dr. W. P. A. JONKER. (Communicated by Prof. SCHREINEMAKERS).

(Communicated in the meeting of February 28, 1914).

1. The adsorption-isotherm is of great importance for the study of the colloids. From various sides efforts have been made to find a connexion between this law and other laws of physical chemistry. Starting from the phase rule and the law of mass action which both can be deduced from the two main laws of thermodynamics, I have tried, in the subjoined lines, to trace the connexion between the adsorption-isotherm, the division rule and the law of constant proportions.

The question whether the phase rule may be applied unreservedly to dispersive systems will not be discussed here.

2. Let us imagine three substances A, B, and C. A and C form two non-mixable phases. C we may call the solvent (dispersive medium). B is soluble in C and can give a "compound" with A. (What kind of compound this is does not matter; it may be a chemical compound or an adsorption compound, or an ordinary solution).

When the equilibrium has set in we have $F = n + 2 - r$; when $n = 3$, $r = 2$ and p and T are constant, $F = 1$, therefore, the system is monovariant (p-T). Which variables can occur here?

A and C form two phases between which B can distribute itself.

Therefore, we are dealing with the concentrations of B in the two phases. If we call the concentration of B in the dispersive medium: c and that in the phase A: $\frac{x}{m}$ (in agreement with the notation used by FREUNDLICH in his "Kapillarchemie") it follows that in the monovariant (p-T)-system $\frac{x}{m}$ must then be $= f(c)$.

3. Only in the case where B in A yields a compound occurring in a separate phase, the system becomes non-variant (p-T), hence

$$\frac{x}{m} = a\ (constant)$$

so that the "compound" is independent of the concentration.

We then speak of a real chemical compound that conforms to the "law of PROUST". This is in harmony with the idea of WALD, who for years has been trying to demonstrate that the constant composition, with which we credit our chemical compounds, is caused by the manner in which we generate these compounds. For we always utilise the occurrence of new phases (distillation, crystallisation, sublimation).

4. As a rule, however, $\frac{x}{m}$ will be a function of c.

The nature of this function may be determined by means of the law of mass action.

We now apply the same to the "compound" which B can form with A and call the number of gram. mols. of A, B and the compound m, p and q, respectively.

Let the formula of the compound be $A_{\frac{m}{q}} B_{\frac{p}{q}}$, then if

$$mA + pB \rightleftarrows q\, A_{\frac{m}{q}} B_{\frac{p}{q}}$$

we get, according to the law of mass action,

$$\frac{C_A^m\, C_B^p}{C_{AB}^q} = k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this only the concentrations in which B appears are changeable.

If again we call C_{AB} : $\frac{x}{m}$ and C_B: c then (1) passes into

$$\frac{c^p}{\left(\frac{x}{m}\right)^q} = k' \text{ or } \frac{x}{m} = a c^{\frac{p}{q}},$$

in which a is constant. If, further, we put $\frac{p}{q} = \frac{1}{n}$ the well known adsorption isotherm

$$\frac{x}{m} = a c^{\frac{1}{n}}.$$

is formed.

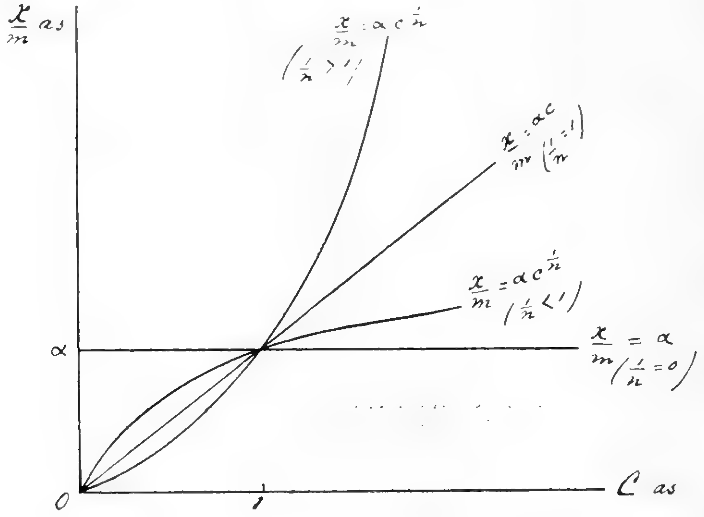
5. This isotherm is generally a parabolic curved line that runs through the origin and the point $(1a)$. From the value

$$\frac{d^2\left(\frac{x}{m}\right)}{dc^2} = a\frac{1}{n} \cdot \left(\frac{1}{n} - 1\right) c^{\frac{1}{n} - 2}$$

we notice that the isotherm will turn the convex side towards the c-axis, when $\frac{1}{n} - 1 > 0$, and the concave side when $\frac{1}{n} - 1 < 0$.

The transition case lies at $\frac{1}{n} - 1 = 0$.

In the subjoined figure the course of the curve has been drawn for different values of $\frac{1}{n}$.



6. For $\frac{1}{n} = 0$, the isotherm passes into $\frac{x}{m} = a$, hence into a straight line parallel to the C-axis. This compound is, therefore, independent of the concentration and consequently a "true chemical compound" obeying the law of PROUST (3).

7. If $\frac{1}{n} = 1$, $\frac{x}{m} = ac$ becomes a straight line through the origin, which cuts the line $\frac{x}{m} = a$ in the point $(1. a)$.

The quantity of the substance B that passes into the phase A is then proportional to the amount of the substance B in the solvent C, in other words, the law of division (HENRY's law applied to two liquid phases) is complied with.

In this case, in $\frac{x}{m} = ac^{\frac{p}{q}}$ (4) p must be $= q$, so that the equation of equilibrium now passes into:

$$m\,A + q\,B \rightleftarrows q\,A_{\frac{m}{q}}\,B,$$

that is to say the substance B has the same number of atoms in the solvent C and in the phase A. This is also assumed in the law of division.

Some investigators are accustomed to speak of a "solid solution" in case the phase A is amorphous-solid. This denomination is likely to lead to confusion with mixed crystals so that, in my opinion, it would be better to use the expression "solution" if one does not like to introduce the word "pseudo-solid".

8. If $\frac{1}{n} > 1$ the convex side of the curve is turned towards the C-axis. We obtain such a line when, for instance, we draw the distribution of acetic acid in water and toluene. In such a case we never speak of "adsorption", but attribute the deviation from HENRY's law to "association".

In fact, from the equation of equilibrium

$$m\,A + p\,B \rightleftarrows q\,A_{\frac{m}{q}}\,B_{\frac{p}{q}}$$

it appears that the substance B passes into the other phase as $B_{\frac{p}{q}}$, and $\frac{p}{q}$ being > 1, the number of atoms has increased.

If $\frac{1}{n} < 1$ we obtain those cases which we are accustomed to call "adsorption". Analogous to (8) we ought to attribute here the deviation from HENRY's law to "dissociation". But nothing of the kind has been found experimentally.

10. Hence, in the above-mentioned matter, I believe I have demonstrated that HENRY's law (law of division) and the law of PROUST are special instances of the adsorption-isotherm. This is in complete harmony with the results of the investigations recently published by REINDERS [1]) and GEORGIEVICS [2]).

Zwolle, February **1914**.

Mathematics. — "*Cubic involutions in the plane*". By Prof. JAN DE VRIES.

(Communicated in the meeting of February 28, 1914.)

1. The points of a plane form a *cubic involution* (triple involution) if they are to be arranged in groups of three in such a way, that, with the exception of a finite number of points, each point belongs to *one* group only. Suchlike involutions are for instance determined by linear congruences of twisted cubics. The best known is produced by the intersection of the congruence of the twisted cubics, which may be laid through five fixed points; it consists of ∞^2 polar triangles of a definite conic (REYE, *Die Geometrie der Lage*, 3e *Auflage*, 2e *Abtheilung*, p. 225). According to CAPORALI [3]) it may also be determined by the common polar triangles of a conic and a cubic. A quite independent treatment of this involution was given by Dr W. VAN DER WOUDE [4]).

In what follows only cubic involutions will be considered possessing the property that an arbitrary line contains one pair only, and is consequently the side of a single triangle of the involution. The

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[1]) Kolloïd. Zeitschr. **13** 96 (1913).

[2]) Zeitschr. f physik. Chem. **84** 353 (1913).

[3]) *Teoremi sulle curve del terzo ordine* (Transunti R. A. dei Lincei, ser. 3*a*, vol. 1 (1877) or Memorie di geometria, Napoli 1888, p. 49). If $a^3_x=0$ and $b^2_x=0$ are those curves, then the involution is determined by $a_x a_y a_z=0, b_x b_y=0, b_y b_z=0, b_z b_x=0$.

[4]) *The cubic involution of the first rank in the plane.* (These Proceedings volume XII, p. 751—759).

lines of the plane are then moreover arranged in a cubic involution. It is further supposed that the points of a triplet are never collinear, the lines of a triplet are never concurrent.

2. If each point P is associated to the opposite side p of the *triangle of involution* Δ which is determined by P, *a birational correspondence* (P,p) will arise. Let n be the degree of that correspondence; then the points P of a line r will correspond to the rays p of a system with index n, in other words to the tangents of a rational curve $(p)_n$ of class n; the rays p of a pencil with centre R pass into the points P of a rational curve $(P)^n$ of order n.

Between the points P of r and the points P^*, where r is cut by the lines p, exists a correspondence in which each point P determines *one* point P^* while a point P^* apparently determines n points P. So $(n+1)$ points P lie on the corresponding line $p = P'P''$.

In that case one of the points P' has coincided in a definite direction p with P, while p has joined with p'. The *coincidences* of the involution (P^3) form therefore a curve of order $(n+1)$, which will be indicated by γ^{n+1}. In a similar way it is demonstrated that the *coincidences* of the involution (p^3) envelop a curve of class $(n+1)$.

When P describes the line r, the points P' and P'' describe a curve of order $(n+3)$; for this curve has in common with r the two vertices of the triangle of involution, of which one side falls along r, and the $(n+1)$ coincidences $P \equiv P'$, indicated above; we indicate it by means of the symbol ϱ^{n+3}.

Analogously there belongs to a pencil of rays with its centre in R a curve of class $(n+3)$, which is enveloped by the lines p' and p'' of the triangles Δ, of which one side p passes through R.

3. The two curves $(p)_n$ and $(p)'_n$ belonging to the lines r and r' have the line p, which has been associated to the point of intersection (rr'), as common tangent. Each of the remaining common tangents b is the side of two triangles Δ, of which the opposite vertices are respectively on r and r'; b therefore bears a *quadratic involution* I^2 of pairs (P',P'').

The pairs (p',p''), which form triangles of involution with a *singular straight line* b, envelop a curve (b). If it is of the class μ, then it has b as $(\mu-1)$-fold tangent, for through a point b passes only one line p'. We call b *a singular line of order* μ. The pairs (p',p'') form a *quadratic involution* on the *rational* curve (b). Its *curve of involution* β, i. e. the locus of the point $P \equiv p'p''$, is a curve of order $(\mu-1)$; for it has with b only in common the points in which this line is cut by the $(\mu-1)$ rays p'', with which $b \equiv p'$ forms pairs of the quadratic involution.

As $\beta^{\mu-1}$ has apparently $(\mu-1)$ points in common with r, b is a $(\mu-1)$-fold tangent of the curve $(p)_n$. Hence b, as common tangent of the curves $(p)_n$ and $(p)'_n$ must be taken into account $(\mu-1)^2$ times. The number of singular lines b satisfies therefore the relation.

$$\Sigma\,(\mu-1)^2 = n^2-1 \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The singular lines b are apparently *fundamental lines* of the birational correspondence (P,p).

The curves $(P)^n$ belonging to the pencils that have R and R' respectively as centres, pass through the point P, which has been associated to the common ray of those pencils. Each point B, which they have further in common has been associated to two different rays p, is consequently a *singular point* of (P^3) and at the same time a *fundamental point* of (P, p).

The pairs of points (P', P''), forming triangles Δ with B lie on a curve (B), which has B as $(m-1)$-fold point if its order is m; then we call B a *singular point of order* m. On this *rational* curve, the pairs (P', P'') form a *quadratic involution*, in which B belongs to $(m-1)$ pairs; the line $p \equiv P'\,P''$ envelops therefore a *curve of involution* of class $(m-1)$.

From this ensues that B in the intersection of two curves $(P)^n$ must be counted for $(m-1)^2$ points, so that the number of points B has to satisfy the equation

$$\Sigma\,(m-1)^2 = n^2-1 \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

4. The involution (P^3) may also have *singular points* A, for which the pairs of points (P', P'') form an involution I^2 on a line a; the latter is then *singular* for the involution (p^3) and the pairs (p', p'') belong to an involution of rays with A as centre; a and A we call *singular of the first order*. The pairs (A, a) are apparently not fundamental for the correspondence (P, p); we indicate their number by α. If $n=1$, as for the involution of Reye, (cf. § 1), then there are only singular points and lines of the first order; for now $n^2-1=0$.

Let us now consider the curves ϱ^{n+3} and σ^{n+3} belonging to the lines r and s. A point of intersection P' of r with σ determines a triangle of involution of which a second vertex P'' lies on s; P'' is therefore a point of intersection of s with ϱ. The third vertex P lies therefore on the two curves ϱ and σ. They have also in common the pair of points that forms a triplet of the (P^3) with the point rs. The remaining points of intersection of ϱ and σ lie in singular points A and B, for they belong each to two triangles of involution, of which one has a vertex on r, the other a vertex on s.

As the singular curve $(B)^m$ cuts each of the lines r, s in m points, ϱ and σ have an m-fold point in B. The numbers m must therefore satisfy the relation $(n+3)^2 = (n+3)+2+a + \Sigma m^2$ or

$$a + \Sigma m^2 = (n+1)(n+4) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In a similar way we find the relation

$$a + \Sigma \mu^2 = (n+1)(n+4) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From the relations[1] (1), (2), (3), (4) ensues moreover

$$\Sigma m^2 = \Sigma \mu^2 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\Sigma (m-1)^2 = \Sigma (\mu-1)^2, \; , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

consequently

$$\Sigma (2m-1) = \Sigma (2\mu-1) \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and

$$a + \Sigma (2m-1) = 5(n+1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

5. The points P', P'', of which the connecting line p passes through E, lie on a curve ε^4, which has a node in E, and is touched there by the lines EE', EE''.

If E is a singular point B then this locus consists apparently of $(B)^m$ and a curve of order $(4-m)$. Hence m may be *four* at most. If $m = 3$, ε^4 degenerates into $(B)^3$ and a *singular line.*

Through E, six tangents pass to ε^4; each of these lines bears a coincidence of the involution (P^3). Such a line belongs to a group of the involution (p^3), in which p'' is connected with p'. The *coincidences* of (p^3) envelop a curve γ_3 of *class three*, reciprocally corresponding to the curve γ^3, which contains the coincidences of (P^3).

By *complementary curve* we shall understand the envelope of the lines p, which form triplets with the coincidences of the (p^3). From what was stated above follows therefore, that the complementary curve of the (p^3) is of the *sixth class.*

Analogously we find a *complementary curve* of the sixth order, $\varkappa^6$, as locus of the points P, which complete the coincidences of the (P^3) into triplets. It has nodes in all the *singular points* of (P^3), for each curve $(B)^m$ and each line a bears two coincidences, which form triplets with the corresponding singular points.

As the curve $(B)^m$ has an $(m-1)$-fold point in B, the curve of

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[1] In my paper "*A quadruple involution in the plane*" (These Proceedings vol. XIII, p. 82) I have considered a (P^3), which possesses a singular point of the fourth order and six singular points of the second order. In correspondence to the formulae mentioned above, $n = 4$ was found.

coincidences γ^{n+1} passes also $(m-1)$ times through B. Consequently γ^{n+1} and $\varkappa^6$ have yet $6(n+1)-2\,\Sigma\,(m-1)$ points in common besides the points B; but these points must coincide in pairs in points where the two curves touch, where consequently the three points of a group of the (P^3) have coincided.

Now

$$2\delta = 6(n+1) - 2\,\Sigma(m-1) = 6(n+1) - \Sigma(2m-1) + \beta,$$

if β indicates the number of points B.

By means of (8) we find further

$$2\delta = (n+1) + \alpha + \beta.$$

Let σ represent the number of singular points $(\sigma = \alpha + \beta)$, we have found then, that the involution (P^3) is in possession of

$$\delta = \tfrac{1}{2}(n + 1 + \sigma)\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

groups of which the three points P have coincided.

Apparently this is at the same time the number of groups of (p^3), which consist of three coincided lines.

If the number of singular points of the order k is represented by σ_k then it ensues from (2) and (8), as $m \leq 4$,

$$9\,\sigma_4 + 4\,\sigma_3 + \sigma_2 = n^2 - 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$7\,\sigma_4 + 5\,\sigma_3 + 3\,\sigma_2 + \sigma_1 = 5\,(n+1). \quad . \quad . \quad . \quad . \quad (11)$$

By elimination of σ_4 we find

$$17\,\sigma_3 + 20\,\sigma_2 + 9\,\sigma_1 = (n+1)\,(52 - 7n). \quad . \quad . \quad . \quad (12)$$

So that it appears that n amounts at most to SEVEN.

6. We shall now further consider the case $n=2$. From $\Sigma\,(m-1)^2 = 3$ follows at once, that (P^3) possesses *three* singular points of the second order $B_k\ (k = 1, 2, 3)$. The curves (B_k) associated to them are conics, which contain involutions (P', P''); the lines p on which those pairs are situated, pass through a point C_k.

The existence of *three* singular straight lines of the second order ensues analogously from $\Sigma\,(\mu-1)^2 = 3$; the points P, which with the pairs on b_k form triangles of involution, lie on a line c_k; the sides of those triangles envelop a conic $(b_k)^2$.

From (8) we further find $\alpha = 6$; consequently there are *six* singular pairs (A, a).

The correspondence (P, p) is quadratic; B_k are its fundamental points, b_k its fundamental lines.

To an arbitrary line r is associated a curve ϱ^5, which has *nodes* in the three points B and in the point associated to r in the quadratic correspondence. The pairs (P', P'') on this *quadrinodal* curve form the only involution of pairs that can exist on a curve of genus *two*; the straight lines p envelop a *conic* [1]).

If r contains a singular point A, ϱ^5 degenerates into the line a and a ϱ^4; the latter will further degenerate as it must possess four nodes, consequently is composed of two conics.

On a *singular line* a lie two coincidences of the involution $I^2 \equiv (P', P'')$; they are at the same time coincidences of the (P^3). The *curve of coincidences* γ is of *the third order*, so a must contain another coincidence. Let it be $Q' \equiv Q$; Q' forms a triangle of involution Δ with A and a point Q'' of a, but moreover a Δ with Q and a point Q^* lying outside a. Consequently Q' is a singular point viz. a point B, for the pairs A, Q'' and Q, Q^* do not lie on *one* line.

The curve ϱ^5 belonging to a consists first of a itself and a conic $(B)^2$; the completing curve must also have arisen from singular points. No second point B lies on a, for this line would then contain four points of the curve of coincidences. Hence two more singular points of the first order lie on a, A^*, and A^{**}. Each *singular line* a contains therefore *two* points A and *one* point B. If a^* cuts the line a in S, then A^* and S form a pair of the involution lying in a; so that AA^*S is a triangle of involution. Hence A is the point of intersection of the singular lines a^*, a^{**}.

7. The connector of two singular points A_k and A_l is not always a singular line a. Let A_l lie on a_k, A_k then forms with A_l and another point Q of a_k a triangle Δ, so that A_kQ is the line a_l. If A_l lies on a_k, a_l passes consequently through A_k.

Let us now consider the line that connects the centres of involution belonging to C_1 and C_2. It contains a pair of points forming a triplet with B_1, and a pair that is completed into a triplet by B_2. Hence it is a *singular line* b; we call it b_3. The axis of involution c_3 belonging to it, is apparently the line B_1B_2; the three lines c form the triangle $B_1B_2B_3$.

In the transformation (P, P') c_3 corresponds with the figure composed of b_3 and the conics $(B)_1^2$, $(B_2)^2$. With γ_3 it has in common the coincidences lying in B_1 and B_2, its third point of intersection with γ^3 lies apparently in b_3c_3. The singular line b_3 is transformed by (P, P') into a figure of the fifth order; to this belongs b_3 itself and the line c_3 twice. As no point B lies on b_3 it must connect

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[1]) The quadrinodal curves ϱ^5 I have treated in "*Ueber Curven fünfter Ordnung mit vier Doppelpunkten*" (Sitz. ber. der Akad. d. Wiss. in Wien, vol. CIV, p. 46—59).

two points A; the correponding lines a form the completing figure.

The conic $(B_1)^2$ has in common with γ^3 the two coincidences of I^2 lying on it and the coincidence of the (P^3) lying on B. As it cannot apparently contain a coincidence of an other I^2 it must pass through B_2 and B_3, while it touches γ^3 in B_1.

8. A conic is transformed by (P,P') into a figure of the tenth order. For the conic $(B_1)^2$ it consists of twice $(B_1)^2$ itself, the conics $(B_2)^2$, $(B_3)^2$ and two lines a; it bears consequently *two* points A, which we shall indicate by A_1 and $A_1{}^*$. As these points each form a triangle of involution with B_1 and another point of $(B_1)^2$, the lines a_1 and $a_1{}^*$ pass through B_1.

Analogously we shall indicate the singular lines which meet in B_2 and in B_3, by a_2, $a_2{}^*$ and a_3, $a_3{}^*$; the points A_2 and $A_2{}^*$ are then situated on $(B_2)^2$; A_3 and $A_3{}^*$ on $(B_3)^2$.

On a_1 two more points A are lying; one of them belongs to $(B_2)^2$, the other to $(B_3)^2$; we may indicate them by $A_2{}^*$ and $A_3{}^*$.

If we act analogously with the remaining points A and lines a, then the sides a_1, a_2, a_3 of the triangle $A_1{}^*A_2{}^*A_3{}^*$ will pass through B_1, B_2, B_3, and the same holds good concerning the sides $a_1{}^*$, $a_2{}^*$, $a_3{}^*$ of the triangle $A_1A_2A_3$.

In connection with the symmetry, which is involved by the quadratic correspondence (P,p), the lines b_1, b_2, b_3 contain respectively the pairs A_1, $A_1{}^*$; A_2, $A_2{}^*$; A_3, $A_3{}^*$. The triangle of the lines b has C_1, C_2, C_3 as vertices; analogously c_1, c_2, c_3 are the sides of B_1,B_2,B_3.

The *six* points A, and the *three* points B form with the *six* straight lines a a *configuration* $(9_2, 6_3)$ B [1]), the points A with the straight line a and the straight lines b the reciprocal configuration $(6_3, 9_2)$ B.

9. That the involution (P^3) discussed above exists, may be proved as follows.

We consider the *congruence* formed by the twisted cubics φ^3, which pass through *two* given points G, G^* and has as bisecants *three* given lines g_1, g_2, g_3 [2]) By h_{kl} and h^*_{kl} we indicate the transversals of g_k, g_l, which may be drawn out of G and G^*.

Let us now consider the net of cubic surfaces Ψ^3, which pass

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[1]) A configuration $(9_2, 6_3)$ A consists of two triplets of lines p_1, p_2, p_3; q_1, q_2, q_3 and the 9 points $(p_k q_l)$.

[2]) This congruence has been inquired into by analytic method by M. STUYVAERT (*"Etude de quelques surfaces algébriques . . . "* Dissertation inaugurale Gand, Hoste, 1902).

through g_1, g_2, g_3 and G^* and have a node in G. The base of this net consists of the 6 lines $g_1, g_2, g_3, h_{12}, h_{23}, h_{31}$; they form a degenerate twisted curve of the 6th order with 7 apparent nodes. Every two Ψ^3 have moreover in common a twisted cubic, which passes through G and G^* and meets each of the lines g_k twice; these curves φ^3 consequently form the above mentioned congruence.

Through an arbitrary point passes a pencil (Ψ^3), hence *one* φ^3. On an arbitrary line l the net determines a cubic involution of the second rank; through the neutral points of this I^2_3 passes a curve φ^3, which has l as bisecant. The congruence $[\varphi^3]$ is therefore *bilinear*.

Through a point S of g_1 pass ∞^1 curves φ^3, they lie on the hyperboloid H^2, which is determined by S, G, G^*, g_2, g_3. All the curves φ^3 lying on H^2, pass moreover through the point S', in which H^2 again cuts the line g_1.

To $[\varphi^3]$ belongs the figure formed by h_{12} and a conic of the pencil which is determined in the plane (G^*g_3) by the intersections of g_1, g_2, h_{12}, and the point G^*. There are apparently 5 analogous pencils of conics besides.

Let us now consider the surface A formed by the φ^3, which meet the line l. Through each of the two points of intersection of l and H^2 passes a φ^3, cutting g_1 in S. From this ensues that the three lines g_k are double lines of A. The lines h_{kl}, h^*_{kl} lie on A, for l for instance meets a conic of the pencil indicated in the plane (G^*g_3), and this pencil forms with h_{12} a φ^3.

We determine the order of A by seeking for its section with the plane (Gg_1). To it belong 1) the line g_1, which counts twice, 2) the conic in that plane, which rests on l and is completed by h_{23}^* into a φ^3, 3) the lines h_{12} and h_{13}, which are component parts of two degenerate φ^3, of which the conic rests on l. From this ensues that A is of the *sixth order*.

10. If the congruence $[\varphi^3]$ is made to intersect with a plane φ, a cubic involution (P^3) arises, which has the intersections of the lines g_k, h_{kl}, and h_{kl}^* as singular points. With the intersection B_k of g_k correspond viz. the intersections of the φ^3, which cut φ already in B_k; they lie as we saw on the intersection $(B_k)^2$ of the hyperboloid H belonging to B_k. To the intersection A_1 of h_{23} corresponds the I^2 on the intersection a_1 of the plane (G^*g_1), originating from the pencil of conics in that plane, etc.

On $(B_1)^2$ lie the intersections of g_1, g_2, g_3, h_{23} and h_{23}^*, viz. the points B_1, B_2, B_3, A_1 and A_1^*; on the intersection a_1 of the plane

$(G^* g_1)$ we find the intersections B_1, A_3^* and A_2^* of g_1, h_{12}^* and h_{13}^*.

To the points P of the line l lying in φ correspond the pairs of points P', P'' lying on the curve of the fifth order, which φ has moreover in common with the surface A^6; this curve passes through the points A_k, A_k^* and has the points B_k as nodes.

So we find a cubic involution possessing the same properties as the cubic involution (P^3) *considered before.*

11. We are now going to consider the case that the plane φ is laid through a straight line c, resting on g_1, g_2, g_3 and cutting these lines in the points B_1, B_2, B_3. The three hyperboloids H determined by these points have the line c in common besides a conic φ^2 through G, G^*, resting on c, g_1, g_2 and g_3 and forming with c a curve of the $[\varphi^3]$. For the conics passing through G, G^* and cutting g_1, g_2, g_3, form a surface of the fourth order, cut by c in a point not lying on one of the lines g. The three hyperboloids mentioned cut φ along three lines b_1, b_2, b_3, meeting in a point C not lying on c, where φ^2 intersects the plane φ again.

The curves $[\varphi^3]$ passing through B_1, meet φ in the pairs of points P', P'', of an involution on b_1. So B_k are now *singular points* of the *first order*. C too is a *singular point* now; for the figure (φ^2, c) has all the points of c in common with φ, so that each pair of c corresponds to C.

The conic $(B_1)^2$ of the general case has been replaced here by the pair of lines (b_1, c); on b_1 lie now the singular points A_1, A_1^*.

The singular points and lines now form a configuration $(10_3, 10_3)$, viz. the well-known configuration of DESARGUES. For in the lines b_1, b_2, b_3, passing through C, the triangles $A_1 A_2 A_3$ and $A_1^* A_2^* A_3^*$ are inscribed, the pairs of corresponding sides a_1^*, a_1; a_2^*, a_2; a_3^*, a_3 of which meet in the collinear points B_1, B_2, B_3.

From the curve ϱ^5, which in the general case corresponds to a line r, the line c falls away; in connection with this the *curve of coincidences* γ^3 passes into a *conic*.

On the ϱ^4 with *one* node D, now associated to r, exists only *one* involution of pairs; the points P', P'', which form triangles of involution with the points of r, lie therefore on the lines p passing through D; consequently $n=1$.

This involution differs from the (P^3) described by REYE only in this respect that the singular point C does not correspond to the pairs of an I^2 on c, as *all* the points of c have been associated to C.

12. Another (P^3) differing in this respect from the involution of REYE, is found as follows. We consider two pencils of conics, which have a common base-point E; the remaining base-points we call F_1, F_2, F_3 and G_1, G_2, G_3. If each conic through E, F_k is brought into intersection with each conic through E, G_k, a (P^3) is acquired, possessing a singular point of the fourth order in E, and singular points of the second order in F_k, G_k [1])

If, however, the points G_k lie on the rays EF_k, then the degenerate conics (EF_1, F_2F_3) and (EG_1, G_2G_3) have in common the line $h_1 = F_1G_1$ and the point $H_1 = (F_2F_3, G_2G_3)$; now H_1 is a singular point corresponding to *all* the points of h_1; consequently it is in the same condition as the point C mentioned above. There are now two more similar points still, $H_2 = (F_1F_3, G_1G_3)$ and $H_3 = (F_1F_2, G_1G_2)$.

While with an arbitrary situation of the points F and G, a ϱ^7 corresponds to a straight line r, which ϱ^7 passes four times through E and twice through F_k, G_k, this curve degenerates now into the three lines $h_k = F_kG_k$ and a ϱ^4, which has a node in the third vertex D of the triangle of involution, of which r is a side. On this ϱ^4, P' and P'' are now again collinear with D, so that $n=1$.

If G_1 is placed on EF_1 and G_2 on EF_2, a special case of a (P^3) is found, where $n = 2$. The curve ϱ^7 now loses only the straight parts h_1 and h_2, consequently becomes a ϱ^5 having nodes in E, F_3, G_3 and D; on this quadrinodal ϱ^5, (P', P'') form again the involution of pairs, so that n appears to be 2. The singular points of the second order are E, F_3, G_3, the singular points of the first order are $F_1, F_2, G_1, G_2, H_1, H_2$; but the last two have respectively been associated to *all* the points of h_1 and h_2, while to each of the first four a quadratic involution corresponds.

13. In the case $n = 3$ we have the relations

$$\Sigma (m-1)^2 = 8 \quad \text{and} \quad a + \Sigma m^2 = 28.$$

The first holds in three ways, for

$$8 = 2 \times 2^2 = 2^2 + 4 \times 1^2 = 8 \times 1^2.$$

But the first solution must be put aside at once. For by (P,P') a line r would be transformed into a ϱ^6; for the connector of two singular points of the 3rd order ϱ^6 would have the two corresponding curves $(B)^3$ as component parts; but then there would be no figure corresponding to the remaining points of the line in question.

The third solution too must be rejected, as, for 8 singular points of the second order $a + 8 \times 2^2 = 28$; so $a = -4$ would be found.

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[1]) See my paper, referred to above, in volume XIII of these Proceedings (p.p. 90 and 91). The notation has been altered here.

For the further investigation there remains consequently the combination of *one* singular point of the 3rd order, and *four* singular points of the 2nd order ; we shall indicate them by C and B_k $(k=1,2,3,4)$. In addition to this we have moreover *three* singular points of the first order A_k.

Then there are further *three* singular lines of the 1st order, a_k, *four* singular lines of the second order and *one* singular line of the third order.

The curve $(C)^3$ belonging to C has in C a node, which is at the same time node of the curve of coincidence γ^4. The two curves have in C six points in common; so also six points outside C; to them belong the two coincidences of the I^2 lying on $(C)^3$; the remaining four can only lie in the points B.

As $(C)^3$ forms part of the curve ε^4 (§ 5), belonging to C, a singular line a_1 passes through C. With γ^4, a_1 has in common the coincidences of the I^2 lying on it, and the two coincidences lying in C; consequently a_1 cannot contain any of the points B. By the transformation (P,P') it is transformed now into a figure of the 6th order, of which $(C)^3$ and a_1 itself form a part; so the figure consists further of the singular lines a_2 and a_3, belonging to two singular points A_2, A_3 lying on a_1.

The singular line a_2 is transformed by (P,P') into a_2, and a figure of the 5th order, arising from singular points on that line. As a_2 does not pass through C and as it must contain, besides the coincidences of the I^2, situated on it, two more coincidences which can only lie in points B, we conclude that it bears two points B_1, B_2 and the point A_1. From this ensues at once, that a_3 too passes through A_1, and contains the points B_3, B_4.

We consider C, B_1, B_2, A_3 as base-points of a pencil (φ^2) of conics; C, B_3, B_4, A_2 as base-points of a second pencil (ψ^2). If each φ^2 is made to intersect with each ψ^2, a (P^3) will arise, having singular points in C, B_k, A_k (see § 12). If to each φ^2 is associated the ψ^2, which touches it in C, then the pencils rendered projective by it, generate the figure $(C)^3 + a_1$; from this it is evident that $(C)^3$ does not only contain the points B_k, but also the singular point $A_1 = (B_1B_2, B_3B_4)$.

It is easy to see now, that A_3B_1, A_3B_2, A_2B_3, and A_2B_4 are the singular lines of the 2nd order. For the φ^2 formed by A_3B_1 and CB_2 is cut by (ψ^2) in a I^2 on A_3B_1 and a series of points (P) on CB_2; so CB_2 is the axis of the involution (p',p'') belonging to A_3B_1.

As the axes of the involutions (p', p''), determined by the four singular lines of the 2nd order pass through *one* point C, the centres of the involutions (P', P'') lying on the conics $(B_k)^2$ will analogously be collinear.

The line on which they lie contains four pairs (P', P''), which form each a triangle of involution with one of the points B_k; from this we conclude that it is the singular line of 3rd order, which (p^3) must have.

14. Let now $n = 4$. As to a line r a ϱ^7 must correspond, no singular point of the 3rd order $S^{(3)}$ can occur beside a singular point of the 4th order $S^{(4)}$ (see § 13). A simple investigation shows that only two cases are possible, viz. (1) *one* point $S^{(4)}$ with *six* points $S^{(2)}$ or (2) *three* points $S^{(3)}$, with *three* points $S^{(2)}$ and one point $S^{(1)}$.

The *first case* appears on further investigation to be realised by the (F^3) mentioned at the beginning of § 12 [1]) To the singular point of the 4th order, E, belongs a rational curve $(E)^4$, which passes also through the remaining singular points F_k, G_k $(k = 1, 2, 3)$. Singular lines of the 2nd order are F_kF_l and G_kG_l; the axes of involutions (p', p'') belonging to them we find in EF_m and EG_m.

As these six axes meet in E, the singular line of 4th order will contain the centres of the involutions I^2 on the conics $(F_k)^2$, $(G_k)^2$.

In the *second case* there are *three* singular points $C_k^{(3)}$, *three* points $B_k^{(2)}$, *one* point A, and, analogously, *three* lines $c_k^{(3)}$, *three* lines $b_k^{(2)}$, *one* line a.

With the curve of coincidences γ^5, which possesses nodes in C_k, $(C_1)^3$ has in common the 2 coincidences of the I^2 lying on it, and six points in C_1; the remaining 7 points of intersection must lie in singular points, consequently $(C_1)^3$ passes also through C_2, C_3, and B_k.

On $(C_k)^3$ lies therefore a point P, which forms a Δ with C_k and B_1; hence $(B_1)^2$ passes through C_k.

The line a is transformed by (P, P') into itself and a figure of the 6th order, so, either into the three conics $(B_k)^2$ or into two curves $(C_k)^3$. But the second supposition is to be cancelled, because a would contain 6 coincidences in that case, two of its I^2 and four in the two points C. Consequently the points B_1, B_2, B_3 lie on the singular line a.

Analogously the singular lines b_1, b_2, b_3 meet in A.

Every singular line c_k passes through a point C_k and completes $(C_k)^3$ into a ε^4.

The curve of the 3rd class $(c_1)_3$ belonging to c_1 has c_2, c_3, b_k as tangents (and c_1 as bitangent).

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[1]) See also my paper, referred to above, in volume XIII, p. 90, 91.

The curve $(b_1)_2$ touches the three c_k (and b_1).

To a conic corresponds in the correspondence (P, P') a curve of order 14; it consists for the conic β_3^2 passing through C_1, C_2, C_3, B_1, B_2, of three curves $(C_k)^3$, of $(B_1)^2, (B_2)^2$ and a singular line. As β_3^2 is the curve of involution of the involution (p', p''), which is determined by that line, it is a singular line of the 3rd order, consequently a line c.

15. For $n = 5$ a further investigation produces only a (P^3) with *six* singular points of the 3rd order and as many singular lines of the 3rd order. Through each of those points C_k passes one of those lines, c_k. A combination of the curve $(C_k)^3$ with the curve γ^6 makes it clear that the first curve also passes through the remaining points C.

To the conic γ_6^2 passing through C_1, C_2, C_3, C_4, C_5 corresponds a figure of the 16th order, composed of the 5 curves $(C_k)^3$, $k \neq 6$, and a singular line, c_6. So γ_6^2 is the curve of involution belonging to c_6.

This (P^3) may be produced by a *net* of *cubic curves* with base-points C_k. All the curves determined by a point P form a pencil, of which the missing base-points form with P a triplet of the involution [1].

16. For $n = 6$ we find as the only solution of the relations (10) and (11) $\sigma_4 = 3$, $\sigma_3 = 2$, $\sigma_1 = 4$. But this is to be rejected. For a conic would have to be transformed by (P, P') into a figure of the 18th order. To the conic passing through 3 points $B^{(4)}$ and 2 points $B^{(3)}$ would correspond the figure composed of 3 curves $(B)^4$ and 2 curves $(B)^3$, which is already of the 18th order.

For $n = 7$ we find no solution at all.

The results obtained are united in the following table

n	σ_1	σ_2	σ_3	σ_4	σ
1	10				10
2	6	3			9
3	3	4	1		8
4		6		1	7
4	1	3	3		7
5			6		6

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[1] This (P^3) is a plane section of a bilinear congruence of twisted cubics indicated by VENERONI (Rend. Palermo, XVI, 210) and amply discussed by STUYVAERT (Bull. Acad. Belgique, 1907, p. 470).

From the relation (9) ensues moreover $\sigma=6$. In all the (P^3) occur therefore *six* groups, of which the three points P have coincided into *one*; in the (p^3) belonging to them *six* groups with united lines p.

Physics. *Further Experiments with Liquid Helium. I. The* HALL-*effect, and the magnetic change in resistance at low temperatures.* IX. *The appearance of galvanic resistance in supra-conductors, which are brought into a magnetic field, at a threshold value of the field*". By H. KAMERLINGH ONNES. Communication No. 139*f* from the Physical Laboratory at Leiden.

(Communicated in the meeting of February 28, 1914).

§ 1. *Introduction, first experiments.* In my last paper upon the properties of supra-conductors, and in the summary of my experiments in that direction which I wrote for the Third International Congress of Refrigeration in Chicago (Sept. 1913, Leiden Comm. Suppl. N°. 34*b*), I frequently referred to the possibility of resistance being generated in supra-conductors by the magnetic field. There were, however, reasons to suppose that its amount would be small. The question as to whether the threshold value of the current might be connected with the magnetic resistance by the field of the current itself becoming perceptible could be answered in the negative, as we had then no reason to think of a law of increase of the resistance with the field other than proportional to it, or to the square of it, and the law of increase of the potential differences at currents above the threshold value could not be reconciled with either supposition. A direct proof that in supra-conductors only an insignificant resistance was originated by the magnetic field was found in the fact that a coil with 1000 turns of lead wire wound within a section of a square centimetre at right angles to the turns round a space of 1 c.m. in diameter remained supra-conducting, even when a current of 0.8 ampère was sent through it. The field of the coil itself amounted in that case to several hundred gauss, and a great part of the turns were in a field of this order of magnitude, without any resistance being observed. The inference was natural, that, even if we should assume an increase with the square of the field, the resistance would probably still remain of no importance even in fields of 100 kilogauss. In my publication (see Report, Chicago, Suppl. N°. 34*b*) I restricted my conclusion about the resistance in the magnetic field to a limit of 1000 gauss, and I also remarked that when it came to making use of the supra-conductors for the construction of strong magnets without iron, it would be necessary in the first place to investigate what resistance the magnetic field would generate in a supra-conductor, and I immediately prepared experiments in connection with this. That I was firmly convinced that the action would be only small, is shown by the fact that I arranged the apparatus for these experiments as if for a phenomenon that could only be studied with profit in fields of 10 kilo-gauss, but it now appears that even then without further preparation, I might have made the observations described below quite easily with the field of 2 kilo-gauss that I then had at my disposal.

For our experiments a coil was prepared as described above, but wound non-inductively. When (17 January 1914) it was brought into a field of 10 kilo-gauss, it showed a considerable resistance. We had not been so successful in the construction of this coil as in the previous one, as it did not become supra-conducting. It was therefore possible that not much value could be attached to this experiment. A coil with tin wire prepared in the same way as the above described non-inductive lead coil also showed a considerable resistance in a field of 10 kilo-gauss when cooled to 2° K., which decreased more slowly than proportionally, when the field was reduced to 5 kilo-gauss. In this case again we had not succeeded in making the coil so that it would become supra-conducting, but (always assuming a regular decrease with the field, and supposing that the fact that the coil did not become supra-conducting only gives a non-essential disturbance) the results of both experiments did not seem to be reconcilable with the above mentioned observations, in which the magnetic field generated no resistance in supra-conductors.

The first thing to do was therefore to repeat the experiments with the coils of tin and lead, which had become supra-conducting in the former experiments, notwithstanding that the windings were in a magnetic field. That these coils were not wound induction-free, was of no consequence, now that it was a question of such comparatively large resistances.

§ 2. *Further experiments with lead and tin which show a sudden change in the resistance at a threshold value of the magnetic field.*

The lead coil of Table XII Comm. N°. 133, as it was not wound induction-free, was placed in the cryostat of the apparatus to be described in a future paper for magnetic measurements in liquid helium, so that the plane of the windings coïncided with the lines of force of the magnetic field which is to be applied. This last acts therefore partly transversely upon the conductor (lines of force at right angles to the current), partly longitudinally (lines of force in the direction of the current).

It was first ascertained that the coil was supra-conducting at the boiling-point of helium. Further that it remained supra-conducting when a current of 0.4 ampère was sent through it; even then the windings were in a not inconsiderable field of their own current.

For further confirmation it was ascertained that the current actually passed through the windings by bringing a small cardanically suspended magnet (pole seeker) near the cryostat; it showed the movements which were to be expected.

Then the magnetic field was applied. With a field of 10 Kilogauss there was a considerable resistance, at 5 Kilo-gauss it was somewhat less. This made it fairly certain that the magnetic field created resistance in supra-conductors at larger intensities, and not at smaller ones. The apparent contradiction that so far had existed between the different experiments, was hereby solved. Later it appeared that 500 gauss was below the threshold value, and 700 above it. Further investigation gave for the resistance (expressed in parts of the resistance at 0° C) as function of the field, the curve that is given diagrammatically completed in fig. 1. The numerical values, in so far as they are necessary for the description of the phenomenon, can be read from the figure, so that they need not be separately detailed here.

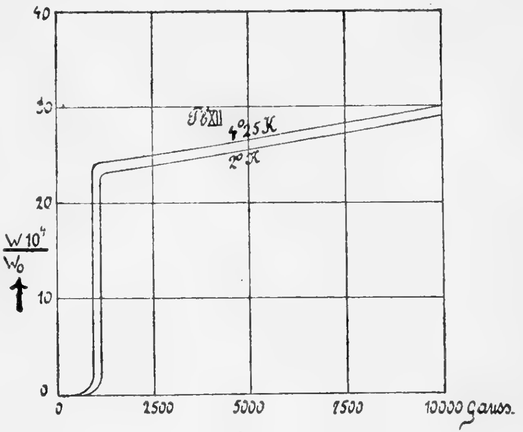


Fig. 1.

It will be seen that the transition from the supra-conducting condition to the ordinary conducting condition through the magnetic field takes place fairly suddenly. The curve, which represents the change of the resistance with the field is closely analogous to that which represents the change of the resistance with the temperature (comp. $I = 0{,}004$ amp. in fig. 7 in Comm. N°. 133). The resistance measurements were made with a current of 0,006 ampère. Of the two curves in fig. 1, one refers to 4°.25 *K*, and the other to 2° *K*. The sudden change in the resistance moves at low temperatures towards higher fields; beyond this point the resistance increases at lower temperatures (2° K.) almost in the same way as at higher ones, it seems as if *the introduction of the magnetic field has the same effect as heating the conductor*.

The tin coil of Comm. N° 133 Table IX was examined in the same way. With this too we have a result in which longitudinal and transverse effects are combined. At 4°,25 *K* the tin is still in a state of ordinary conductivity, the curve, which represents the resistance as a function of the field decreases in steepness (see fig. 2) with a diminishing field and meets the axis of ordinates pretty nearly parallel to the axis of abcissae. The only thing, therefore, that is remarkable here as compared to what is observed at higher temperatures, is the decrease of the slope to zero. There is no indication of a sudden change.

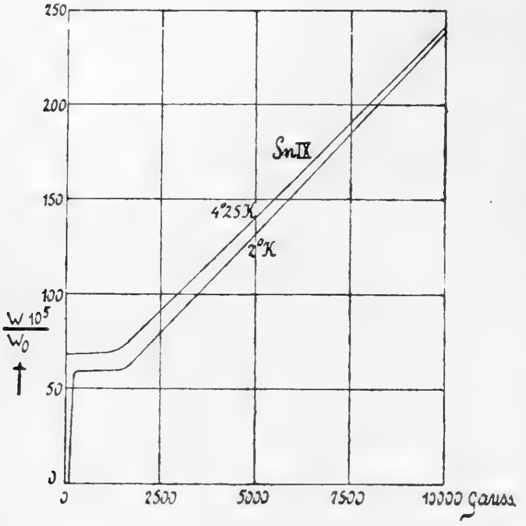


Fig 2.

With the supra-conducting tin at 2° *K* we find, as with lead a sudden change, in this case at the threshold value of 200 gauss. In fact with tin at 2° *K* we are much nearer to the temperature of sudden change for the resistance (3°,8 *K*) than in the case of lead (sudden change for the resistance 6° *K* (?) (comp. Comm. N°. 133).

§ 3. *Separate observations of the longitudinal and of the transverse effect with lead.*

Pressed lead wire was wound on a plate, so as to cover it with a few flat layers of insulated windings. The windings could be so directed that the effect was entirely transverse, or almost entirely longitudinal. The results for the temperatures of 2° *K* and 4°.25 *K* are given in the four curves in fig. 3.

The sudden change in both effects takes place almost at the same threshold value of the field. The longitudinal effect is weaker than the transverse effect. The value of the effect at hydrogen temperatures was examined by Dr. K. Hof and myself, and I take this opportunity to thank him

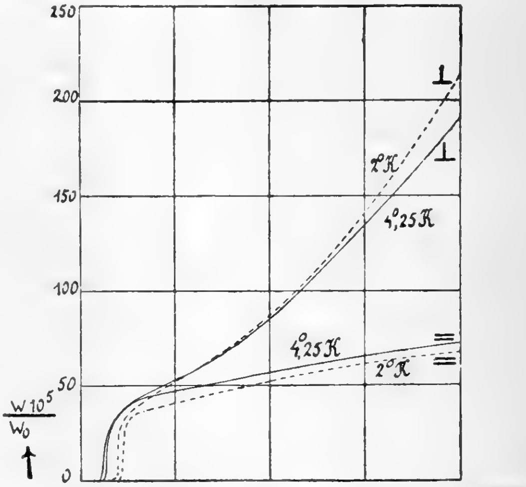


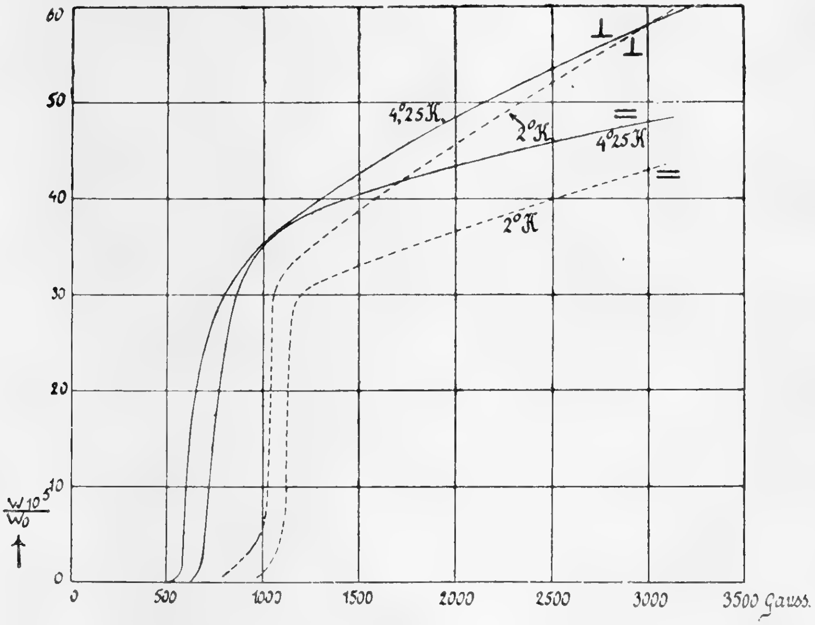
Fig. 3.

for his help. A paper on the subject will be published shortly. It appears from this that the effect which (see fig. 3, and in detail fig. 4) changes little with the fall from 4°.25 K to 2° K, increases considerably with the fall from 14° K to 4°,25 K.

It is worthy of notice that the sudden change *differs considerably in magnitude* with Pb_{XII} and Pb_{f1}. Possibly there is a difference in the nature of the lead in the two coils. In fact at 20° K

$$\frac{W_{PbXII}}{W_0} = 0{,}0284 \text{ and } \frac{W_{Pbf1}}{W_0} = 0{,}0274.$$

Amongst the different questions that arise, one is whether a lead wire might be constructed in which the magnetic resistance, remaining zero as far as the threshold value of the field, will further gradually increase with the field from the value 0 upwards.



Fig, 4.

There is no doubt that the phenomenon discovered here is connected with the sudden appearence of ordinary resistance in the supra-conductors at a certain temperature. The analogy between the influence of heating upon the resistance and that of the introduction of the magnetic field, is so far complete.

One would be inclined to assume that an energy of rotation determined by the magnetic field might be simply added to the energy of the irregular molecular motion. If, in the production of the obstructions which determine the resistance we have to do with dissociations in the sense, that movements of electrons in certain paths become unstable at a definite temperature, the magnetic centrifugal force might make there motions one-sidedly unstable at another temperature.

If the creation of ordinary resistance in supra-conductors with currents above a certain threshold value, which is fully described in Comm. N°. 133, really is a peculiarity of the supra-conducting metal, and not due to disturbances, then the new phenomenon might also be connected with this property. In fact if it were once proved — to use an image already introduced into my paper for the Congress in Chicago — that the vibrators which cause the resistance can only be set in motion when the stream of electrons passes them with sufficient rapidity, then it would not be surprising that the magnetic resistance does not arise until the rapidity of the circulating motions of the electrons is great enough to carry the atoms with it and set them in rotation, by which they can then disturb the regular motion of the electrons.

Finally, it is certain that the phenomenon described is connected with the laws of magnetisation of supra-conductors which are as yet unknown.

Before however drawing definite conclusions from the new phenomenon, it is desirable to gather more experimental information on the subject.

Physiology. — *"Electrocardiograms of surviving human Embryos"*. By Prof. J. K. A. Wertheim Salomonson.

(Communicated in the meeting of February 28, 1914).

By the kindness of Dr. H. Treub, Professor of Obstetrics and Gynaecology I was enabled to record the electrocardiograms of 3 human embryos, born after operation for extrauterine pregnancy etc. The age of the embryos was given as about 6 weeks, 5 months and 8 weeks and agreed with the length measurements.

As the operations were performed in the University Institute for Obstetrics and Gynaecology, the embryo had to be sent to my laboratory in the University hospital about one mile distant, there being no telecardiographic connection between the two.

The embryo was put into a bottle containing a warm solution of Ringer. In the laboratory it was immediately placed in the hot moist chamber, which I had formerly used for my experiments with chicken embryos. The leads to the Einthoven galvanometer were placed on the upper part of the thorax and on the abdomen.

The first embryo gave only a few rather poor tracings. I suppose that its early stage of development, the effects of the shaking during transport and perhaps of a change of temperature may have been the cause. From the second and third embryo I got a series of satisfactory tracings.

I may be allowed to show first the tracings from the last embryo, which were obtained on a plate moving 20 mm. a second, an enlargement of 1100 times, and a string of high resistance and sensibility adjusted to a 30 mm. deflection for 1 millivolt.

Looking at the tracings we immediately see that the heart action was not entirely regular. The interval between two contractions is not equal. The complexes occurring with every heart-beat also showed a notable difference. In the first tracings we see two different forms, alternating regularly. A little later an intermediate form occurs a few times and in the last negatives we see only one of the first complexes. As a point of interest we note the complete absence of waves which might be identified as *P*-waves.

The different complexes bear a decided resemblance to heterogenetic complexes occurring after stimulation of the right and left ventricle. A contraction showing the form of a *B*-complex in which there is a lesion of the right bundle, is followed each time by a complex of the *A*-type, where the contraction is caused by stimulation of the right bundle or the right ventricle.

Already in the fourth negative we see *B*-complexes which are not followed by an *A*-complex. In the 5th negative we find for the last time two complexes slightly resembling *A*-types, but with a much smaller amplitude and a few particulars that cause them to be considered as intermediate or *C*-types. After this we see only *B*-complexes with a very slowly decreasing amplitude. The last tracings become very irregular and show many small anomalous complexes of different types.

In the second embryo, measuring 26 centimetres, the thorax had been opened by Prof. Treub, who was in doubt if the heart was still beating. Here the contractions came in groups of 10—20 or even 2—5 single beats, in the same way as was seen with chicken embryos.

The curves were traced with a velocity of 25 mm. per second; the sensibility was adjusted at 10 mm. per millivolt.

All the contractions showed atypical complexes of the *B*-form starting with a descending curve, rising afterwards. Generally the first contraction in a group was a rather small one, the next ones being somewhat larger. The groups ended abruptly.

The first descending part in such a complex was generally interrupted by a few short waves, after which the descent became regular. The ascending part was less steep and ended in a blunt summit. Before this last wave sometimes a small intermediate wave could be detected.

About 10 minutes later between the regular complexes as described above, other anomalous ones appeared, of a much longer duration. The number of these grew, and the form first observed disappeared entirely. At last the tracing showed merely a series of continuously changing, very abnormal complexes.

It is difficult to explain these tracings. We know of course that they are related to extremely abnormal circumstances. We have before us a heart, very imperfectly developed, the halves of which freely communicate, the ductus Botalli still being largely open. An embryo with such a heart is asphyxiated without the possibility of a normal large or small circulation, as at the same time the circulatory system is entirely void of blood, and the heart cannot pump any other fluid into the placentary or proper circulatory system. The consequences are not, even approximately, to be foreseen. We can only consider one or two points.

The normal stimulus for the heart starts near the right venous sinus. But in the long run this necessitates the presence of blood in the vessels. If this is and remains absent, the sinus node stops its work. In such a case other parts of the auriculo-ventricular bundle may temporarily continue the work. In the embryo n°. 3 we find the evidence, that this occurs alternately in the left and right part of the bundle, and later on only in the left part. The result is a ventricular automatism. At last the left part of the bundle also breaks down, but at this moment the overworked muscle contains so much fatigue-products as to cause a "diathèse de contracture", and to produce idiogenetic irregular ventricle contractions, originated in the muscle-substance itself without the aid of the bundle of His-Tawara. In the larger second embryo, with the exposed heart these irregular spasmodic contractions occurring at the same time as the lengthened complexes could easily be seen.

If the complexes produced by the second embryo may be considered as to be caused by a temporary ventricular automatism, the small waves in the commencement of the first descending part of the wave may be taken as recurrent auricular waves. As these commence about the same time as the ventricular complexes, the starting point of the stimulus ought to be situated not in the ventricle itself, but somewhere between the auricle and the ventricle.

In the common well-known atypical complexes of the B-form we never see this recurrent wave and in the rare clinical cases with recurrent auricle wave it is seen after the R-wave. Though this seeming discrepancy can be accounted for, we may perhaps find a fuller explanation after a continued research.

Geology. — *"On homoeogeneous inclusions of Kawah Idjen, Goentoer and Krakatau and their connection with the surrounding eruptive rocks."* By H. A. Brouwer. (Communicated by Prof. G. A. F. Molengraaff.)

(Communicated in the meeting of February 28, 1914).

From the study of homoeogeneous inclusions of eruptive rocks it is apparent which rocks of great depth may crystallize out of the mothermagma, and to which differentiations this magma was subject during the formation of a certain volcanic complex, even when the eruptive aequivalents of certain products of differentiation, occurring among the inclusions, are not known among the volcanic rocks of the complex. Further, they show us the conditions of crystallization of certain minerals, which only under special conditions can be formed out of a magma of a certain chemical constitution [1]). For the determination of the relative age of rocks of the same volcanic complex the study of inclusions is an important resource, especially for the Indian volcanoes, which for the greater part are built up from loose rolled material, natural denudations being of little occurrence.

Kawah Idjen.

The volcanic products of the Kawah Idjen [2]) consist chiefly of cinders and stones, which are partly hardened into a conglomerate and are beautifully denudated in the precipitous walls that surround the lake of the crater. Somewhat above the locks of the irrigation which when the level is high unloads the lake, there begins a flow of lavas that follows the left shore of the drainage. Along the precipitous slope to the locks and in the stream of lavas, during a short visit in August 1912, some homoeogeneous and enallogeneous inclusions were collected. The enclosing rocks are hypersthene-augite-andesytes, in which numerous light-coloured phenocrists of plagioclase form a contrast with the gray to grayish black glassy groundmass.

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[1]) A. Lacroix, Les enclaves des roches volcaniques Mâcon 1894. Id. La Montagne Pelée et ses éruptions, Paris. 1904.

[2]) R. D. M. Verbeek and Fennema, Java en Madoera. I. p. 81. Amsterdam 1896.

Microscopically examined these plagioclases show kernels from labradorite to bytownite, and a repeated alternation of more basic and acidic layers; besides pale green augite which sometimes occurs as twin crystals according to (100), and hypersthene with a distinct pleochroism in pale green and pale brownish-yellow colours, we occasionally also remark small ore-crystals among the phenocrists. The glassy base is partly unglassed, and contains edges of plagioclase, small pillars of both augite and hypersthene, and ore-crystals.

The homoeogeneous inclusions are partly holocrystalline micropyroxene diorites, partly they only differ from the surrounding rocks by the strong increase of the crystals of plagioclase, augite, hypersthene and ore in the groundmass, whereas the glass only occurs caught between the crystalline constituents; they apparently have formed crystalline parts in the rising magma, their total crystallisation occurring simultaneously with that of the surrounding lavas. The microdiorites are partly rather abundant of ore and then appertain to a cleavage product more basic than the surrounding lavas. Exceptionally olivine, in a small quantity, was found among the constituents of these inclusions while it is wholly absent in the examined samples of the surrounding pyroxene andesites. The occurrence of olivine indicates cleavage products of the common mothermagma in which this mineral may crystallize, these cleavage products being known to us from the olivine-containing pyroxene andesites and basalts of volcanoes of the same complex [1]. (Merapi, Raoeng, Gd. Pondok, Koekoesan).

Goentoer.

During the ascension of the Goentoer in April 1913 a scattered vegetation turned out to have reached the very top, whereas Verbeek, on the smooth cone that has but few incisions even now, did not meet with a single trace of vegetation above the limit af 1000 m. The rocks of the Goentoer complex, as far as they have been examined by Lorié, Behrens, Verbeek, and myself, are chiefly basalts, that sometimes graduate into olivine-containing andesites, andesites without olivine also occurring. The products of the youngest point of eruption (the Goentoer properly speaking) which now only at the northwestern side shows some vapor of water and SO_2 rising from it, but which during the preceding century was frequently very active, consist of streams of lavas and gravel, or big blocks of often very porous rocks, which entirely cover the upper part of the streams of lava. As far as they have been examined, they are all found to be olivine basalts,

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[1] R. D. M. Verbeek and Fennema, loc. cit.

usually with numerous phenocrists of plagioclase, sometimes besides green augite also hypersthene occurring among the phenocrists.

The homoeogeneous inclusions have been gathered in porous fragments along the slope above the hot springs of Tjipanas, near the brink of the crater. They are chiefly rather fine-granular olivine gabbroes, which by their pale colour distinctly contrast with the dark lava. The percentage of olivine varies, but is usually rather high. Some of the inclusions consist of basic plagioclase, green augite, olivine and magnetite; the olivine crystals with more or less rounded edges are often entirely surrounded by the augites, the latter being angularly bounded with respect to the plagioclases. Hypersthene being among the constituents there arise graduations into particular inclusions in which augite is absent among the constituent minerals, a strong brownish-black to brownish-yellow pleochroitic amphibole and hypersthene both occurring in its place. In these inclusions also, the plagioclase is rather well idiomorphically developed with respect to amphibole and hypersthene, whereas olivine-crystals with rounded edges and sometimes irregularly shaped are entirely enclosed by amphibole and hypersthene. All these rocks represent shapes of different depths of olivine-basalts, the amphibole seems to be absent in the effusive aequivalents and was either not produced, the circumstances of crystallization being different, or it was wholly resorbed after crystallization. On the contrary, the rounded shape of the olivine-crystals with their spread framing by amphibole, indicates a resorption of the first-mentioned mineral in the holocrystalline rocks. The inclusions without augite show a rare combination of minerals by the absence of monoclinic pyroxene and the presence of olivine, this mineral generally being absent in amphibole gabbroes and similar rocks.

Olivine-free inclusions are the aequivalents of more andesitic rocks, which we know from other parts of the Goentoer complex. In a similar inclusion there were recognized: plagioclase, both hypersthene and augite, and magnetite. As a rule the plagioclases form the bigger individuals not limited idiomorphically, which in a very large number poikilitically surround small pyroxene crystals.

Krakatau.

During a visit to Krakatau in the beginning of May 1913, in one of the basaltic windings west of the great winding of hypersthene andesite [1]) angular fragments were collected of a light-coloured fine- to coarser-granular rock, which microscopically examined turned

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[1]) R. D. M. VERBEEK, Krakatau, II, p. 160. Batavia 1885

out to contain much quartz. Although acidic hypersthene andesites mark the first and third period that **Verbeek** distinguishes in the history of the volcano, the quartz has not been able to develop itself as such, under the circumstances in which these rocks crystallized, and is found in virtual state in the glass of the groundmass.

The surrounding basalt contains phenocrists of basic plagioclase and a small quantity of olivine in a glassy mass with crystals of more acidic plagioclase, augite and ore. The holocrystalline inclusions of which the largest dimension measures 10 cm. consist of strongly zonair plagioclases, quartz (a good deal of it fine-granophyrically grown together with feldspar), worn dark minerals and ore. In the fine-granophyrical conglomerations also kali-feldspar may be found. The SiO_2 percentage varies, the chemical constitution of one of the inclusions appearing from the following analysis (analyst F. G. **Mannhardt**):

SiO_2	64,14
TiO_2	4,86
Al_2O_3	14,91
Fe_2O_3	3,41
FeO	3,64
CaO	5,69
MgO	0,82
Na_2O	1,67
K_2O	0,91
H_2O	0,68 [1]
Sum total	100,73

Calculating the analyses according to the American system we find a remarkable high percentage of SiO_2 that is not bound as a silicate (about 38 %).

It appears from the above-said that the homoeogeneous inclusions of the Kawah Idjen, according to their chemical constitution, show but a few varying types; in connection with this fact the chemical constitution of the andesites and basalt of the Idjen complex differ but slightly. [2]

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[1] Loss by ignition.

[2] The basalt of the stream of lavas of the Merapi which flows into the sea near Batoe Dodol on the straits of Bali contains (according to **Stöhr**) 54 % SiO_2; two pyroxene andesites of the Kawah Idjen contain 58 % and 60 % SiO_2; and among the rocks that were gathered by me during the eruption of the Raoeng in 1913, on the northern slope of the volcano near the brink of the crater, some amphibole-hypersthene-augite-andesites with 63 % SiO_2 occur. Also the olivine-containing basaltic cinders of the youngest Raoeng-eruption have a high SiO_2 percentage (54 %).

Various aequivalents of the basalts and aequivalents of the andesitic rocks of the Goentoer in a broader sense were found among the homoeogeneous inclusions of the youngest eruptive products of the Goentoer properly speaking.

The quartz-containing inclusions of the basalts of Krakatau illustrate the presence of virtual quartz in the groundmass of the hypersthene andesites of the first period, and would as well be the only traces of differentiation in the mother-magma before the basaltic eruptions, if not, not only the greater part, but all traces of the former basic eruptions had disappeared by a fall-down.

The occurrence of augitefree plagioclase-hypersthene-amphibole-olivine rocks as homoeogeneous inclusions in the products of the Goentoer teaches us that such combinations of minerals may at a greater depth crystallize out of the basaltic magma.

It appears from the calculation of the norm that also the quartz-containing inclusions of Krakatau belong to the rare combinations of minerals because, according to the analyses calculated by Washington no other rock belongs to the sub-class (II. 3, 4, 3).

Chemistry. — *"On the pyrophoric phenomenon in metals"*. By Prof. A. Smits, A. Kettner, and A. L. W. de Gee. (A preliminary communication). (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of February 28, 1914.)

In a previous communication [1]) it was pointed out that the pyrophoric phenomenon would possibly have to be explained by this that the metals obtained in the reduction of certain compounds are comparatively far from the state of internal equilibrium and show an abnormally great power of reaction in consequence of an abnormally large content of the simpler kind of molecule.

The explanation for this phenomenon prevalent up to now, which is of more frequent occurrence than is perhaps supposed (we found it with Cu, Bi, Pb, Ni, Fe) attributed the great reactive power to the very finely divided state; so an explanation which is perfectly analogous to that of the so called "chemical flag" for phosphorus

Now the possibility might also be considered that in the liberation of the metal a pyrophoric admixture is formed, or that the hydrogen

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[1]) These Proc. XVI, p. 699.

dissolves somewhat in the metal or becomes denser on the surface and exercises a catalytic influence.

It has, however, appeared that pyrophoric iron may be obtained when different iron compounds are heated for a short time in a hydrogen current at ± 350°. This succeeds with ferro oxalate, ferro tartrate, ferro chloride, and with the oxides of iron, from which follows that no common admixture except hydrogen can be pointed out here, to which the pyrophoric property could be ascribed. Now it appeared, however, that also pyrophoric iron can be obtained when ferro oxalate is heated *without* contact with hydrogen, which proves that the hydrogen certainly does not cause the pyrophoric phenomenon. [1])

To test the supposition expressed by one of us, it was examined in the first place what the influence is of the temperature on the pyrophoric phenomenon. Sealed to glass tubes with pyrophoric iron were placed in a thermostat, which was regulated at different temperatures between 250° and 340°. After a certain time the tubes were taken from the bath and opened to find out if the iron was still pyrophoric. The result is given in the following table:

Duration of the heating	Temperature	Result
a week	250°	still pyrophoric
„ „	290°	no longer pyrophoric
48 hours	310°	hardly pyrophoric
24 „	340°	no longer pyrophoric

The pyrophoric property of iron, therefore, vanishes with heating to higher temperature. The rapidity with which this happens, increases greatly with the temperature. 310° is about the temperature at which the conversion has taken place almost completely in **48** hours.

That at this temperature a massing together of the powder should have taken place, and that in consequence of this the pyrophoric phenomenon would have disappeared, is pretty well out of the question, and it was therefore of importance to make an attempt to examine whether the transition *pyrophoric iron* → *non-pyrophoric*

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[1]) THIEBAULT [Bull. Soc. Ch. de Paris (3) **31**, 135] found that when Bi-mellate is heated in vacuo, pyrophoric Bi is formed; in the same way we obtained pyrophoric Bi from the citrate.

iron is attended with a variation of volume, as in this way an important support might be given to the supposition of an internal transformation.

In a dilatometer constructed specially for the purpose Fe_2O_3 was reduced with hydrogen under such circumstances (temp. and time) that on the ground of experiments, previously taken, the iron could certainly be assumed to be pyrophoric. Then the apparatus was exhausted and filled with mercury, which had been boiled at the airpump [1]).

In connection with the experiments in sealed to glass tubes it was to be expected that in case of one or two days' heating nothing could be observed until the neighbourhood of 300° is reached. In agreement with this the following was found:

Temperature	Duration of heating	Change of position of the mercury meniscus
212°	54 hours	0 cm.
284°	22 „	0,2 „
320°	48 „	+14 „ On continued heating no change of volume took place any longer [2]).

Accordingly it appeared most convincingly from the dilatometric investigation that a considerable increase of volume takes place exactly in the temperature region where the pyrophoric property of the iron vanishes with such rapidity that it can no longer be demonstrated after ± 48 hours. In virtue of these preliminary experiments it may, therefore, be considered as certain that the transition of pyrophoric iron to ordinary iron is accompanied with an increase of volume. The supposition that pyrophoric iron is iron that is not in internal equilibrium, has thereby greatly gained in probability. In a subsequent communication it will be demonstrated why pyrophoric iron must not be considered as a new modification of iron.

Amsterdam, Febr. 27, 1914. *Anorg. Chem. Lab. of the University.*

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[1]) Iron and mercury were examined after the experiment was over, when the mercury appeared to contain only exceedingly small traces of iron, and the iron to be perfectly free from mercury.

[2]) At the end of the experiment the iron appeared to be no longer pyrophoric.

Chemistry. — "*Answer to* Prof. E. COHEN *to his observations under the title of Allotropy and Electromotive Equilibrium*". [1]) By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of Feb. 27, 1914).

Mr. COHEN's attack under the title of "Allotropy and electromotive Equilibrium" induces me to make the following remarks.

Mr. COHEN seems to think it anything but correct that I have ventured to enter a field of work, which had been proclaimed his territory of research in more than one address, treatise, and magazine.

This deed, however unpardonable it may appear in Mr. COHEN's eyes, may be very reasonably accounted for. If I had not seen a chance to throw new light on the phenomenon of allotropy, I should certainly not have occupied myself with it, as it would not have prompted me so urgently to investigation then, but when a few years ago I came to the conviction that the phenomenon of *enantiotropy* and *monotropy* and the allied phenomena might be united under a new point of view, by the assumption that every phase of an allotropic substance is built up of different kinds of molecules, I did not hesitate for a moment, but immediately set about to test the drawn up theory with my pupils. This is the reason that of late years I have studied the phenomenon of allotropy, and I do not think that there is anything in the line of conduct followed by me that can in the least rouse astonishment.

Further Mr. COHEN considers it necessary to point out that the form of my publications might give rise to misunderstanding, which would appear from a passage occurring in my latest paper [1]), running: "In connection with the foregoing it is desirable to draw attention to this that according to these considerations the contact with the solution of a salt of the metal must have an accelerating influence on the setting in of the internal equilibrium of the metal."

MR. COHEN has taken offence at this sentence, because according to him I should have forgotten to mention that already fifteen years ago this fact was found by him and VAN EYK, and has since been explained by him.

This remark of Mr. COHEN is *very significant*, for I do not think that he could have made it apparent in a clearer manner that the contents of my communication "The application of the theory of allotropy to electromotive equilibria" have remained *perfectly* dark to him.

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[1]) These Proc. XVI p. 708.

Messrs. Cohen and Van Eyk [1]) found that when e.g. white tin is left in contact with a tin solution at a temperature lying under the transition point, the conversion of the metastable white to the stable grey tin is accelerated. Mr. Cohen's explanation is this [2]) that when once a trace of grey tin is present, the tin from the solution will deposit in the grey modification on the grey tin, in consequence of the difference in "Lösungstension" of white tin and grey tin, the white tin entering the solution. It is clear that all this refers to the conversion of one modification to another or of one solid phase to another.

My paper does not deal with the transformation which takes place between two solid phases of an allotropic substance, but with *the chemical conversion which can occur between the different kinds of molecules in each of the solid phases according to the theory of allotropy.*

In the cited communication I namely pointed out that the just-mentioned theory states that a metal which presents the phenomenon of allotropy, will contain different kinds of molecules. To simplify the case as much as possible I assumed that double molecules M_2 occur by the side of simple molecules M. If the metal is now to behave as a substance of one component, so in a unary way, it is necessary that the different kinds of molecules in each of the phases of the metal are in equilibrium, and as we have to do here with an equilibrium between the kinds of molecules of one and the same substance, the word "internal equilibrium" is used here to distinguish it from other equilibria.

Up to now it has always been assumed that a metal emits only one kind of ions into solution. In connection with the just-mentioned internal equilibrium in the homogeneous metal phase we come, however, to the conclusion that the metal supposed here immersed in an electrolyte will emit different ions, which, if the ion per atom carries e.g. three positive charges, will be the ions $M^{\cdot\cdot\cdot}$ and $M_2^{::::}$.

Just as the molecules M and M_2 in the homogeneous metal phase can be in equilibrium, this will also be the case for the ions $M^{\cdot\cdot\cdot}$ and $M_2^{::::}$, and this equilibrium, too, may be called an internal equilibrium.

Now I have among others pointed out that the metal can be in unary electromotive equilibrium only when the different kinds of

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[1]) Zeitschr. f. phys. Chem. 30, 601 (1899).

[2]) „ „ „ „ 30, 623 (1899).

molecules in the metal and the different kinds of ions in the electrolyte each in itself, are in internal equilibrium.

It is to be expected that at the ordinary temperature the internal metal ion equilibrium sets in rapidly, whereas the metal in itself at the ordinary temperature does not pass into the state of internal equilibrium, or only exceedingly slowly.

When, however, the metal is brought into contact with an electrolyte which contains the ions of this metal, the surface of the metal, as I have demonstrated, will assume internal equilibrium in consequence of this that more of those ions in which the metal is deficient, deposit as molecule from the electrolyte, or that the metal sends more of those molecules as ion into solution which have too great a concentration in the metal. These two processes, which dependent on the concentration of the metal can also proceed simultaneously, bring about that the concentration of the surface of the metal becomes equal to that which corresponds to the internal metal equilibrium at the given temperature and pressure. In the maintaining of this equilibrium between the molecules M and M_2, as well as in its setting in, the electrolyte as connective link, will play an important part.

So it appears convincingly from what precedes, just as from my previous communication that the quoted passage refers to the transformations which take place when a metal phase which is not in internal equilibrium, passes into the state of equilibrium.

Also where I mention the transition point, I have said: "At the point of transition the electrolyte will greatly promote the internal equilibrium both in the metal *e*, and in the metal phase *d* for the just-mentioned reasons."

The case referred to by Mr. COHEN, the influence of an electrolyte on the conversion of one modification to another, I have therefore left entirely *out of consideration*, and as it is not exactly practical to mention the names of those who have occupied themselves with *other* phenomena, there was no occasion for me to mention Mr. COHEN in my preceding paper.

This *will*, however, be the case when I shall discuss also the influence which Mr. COHEN has in view, when it will appear that a deeper insight is attained just by means of the considerations given in my preceding communication.

In conclusion in reference to the motive of Mr. COHEN's attack, which according to him is to be found in the fact that more and more both Dutch and foreign colleagues should have objected to the line of conduct followed by me, I will only remark that different Dutch colleagues have expressed their sympathy with my work to me. And as Mr. COHEN also mentions foreign countries, I may add that I have, indeed, carried on a controversy with Mr. TAMMANN, from which it therefore appears that on that side, as I had, indeed, expected, I meet with opposition; but I may state that on the other hand both before and after this controversy I have received expressions of great sympathy with my views from very competent colleagues from Germany, Sweden, England, and America, expressed in letters or publications, which if this should be considered desirable, I shall be glad to lay before the Committee of this Academy.

Amsterdam, Febr. 1914.

(April 23, 1914.)

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING of Friday April 24, 1914.

VOL XVI.

President: Prof. H. A. LORENTZ.
Secretary: Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Vrijdag 24 April 1914, Dl. XXII).

CONTENTS.

Botany. — *"On the Regulation of the transpiration of Viscum album and Rhipsalis Cassytha". A contribution to the knowledge of the antagonism between the guard cells of the stomata and the adjacent cells of the epidermis.* By Z. Kamerling. (Communicated by Prof. Beijerinck).

(Communicated in the meeting of Jan. 31, 1914).

In recent years I have conducted numerous experiments to obtain an insight into the need for water and the consumption of water in various tropical plants. In continuation of these investigations, carried out in Java and in Brazil, similar experiments have been undertaken during the last few months in Holland with native plants. The method of inquiry was almost always the same: leafy boughs were cut off and hung up in the laboratory in the shade or exposed to the sun in the habitat of the plant investigated; they were weighed periodically at shorter or longer intervals.

By this method of experiment the extent of transpiration can be determined when the tissues of the plant still possess their normal water-content and also the nature of its modification, when the tissues of the plant gradually lose water.

These experiments show that in many plants there is a continuous and very considerable transpiration from the beginning of the experiment until the leaves of the bough are dried up. In other species the transpiration is more or less great at the beginning, but decreases gradually so that finally it sinks to a minimum-value. This decrease or regulation of transpiration is evidently due to the narrowing or closing of the stomata, which in the different plants investigated may occur more or less quickly and more or less extensively.

In some plants I found that in contrast to the normal course of the regulation, the intensity of transpiration increases distinctly at the beginning and only afterwards diminishes in the usual way. Such an irregularity, at least when there is no external influence at work, such as temperature, illumination or conditions of humidity or movement of the atmosphere, can hardly be explained otherwise than by assuming that the aperture of the stomata in these cases first dilates when the plant begins to wither and only afterwards constricts.

I observed this phenomenon very clearly in *Viscum album* in a comparative experiment which I performed on the transpiration of this plant and of some deciduous and evergreen woody plants.

It is unnecessary to publish here the detailed results. I append only the figures which have reference to the above-mentioned irregularity in the regulation of transpiration.

The boughs for experiment were arranged at an open window, where they were not reached by the sun before mid-day, and only for a short time afterwards.

6 September	First bough experimented on Viscum album. Weight in grammes	6 September	Second bough experimented on Viscum album. Weight in grammes	6 September	Third bough experimented on Viscum album. Weight in grammes
9.25	21.5 grm.	9.35	15.75 grm.	9.40	15.55 grm.
9.45	21.2 „	10.	15.55 „	10.	15.50 „
10.10	21.0 „	10.15	15.4 „	10.20	15.42 „
10.45	20.7 „	10.55	15.0 „	10.55	15.24 „
11.15	20.27 „	11.25	14.57 „	11.25	14.94 „
11.45	19.82 „	11.55	14.12 „	12.	14.53 „
2.	18.3 „	2.15	13.22 „	2.15	13.15 „
3.35	17.2 „	3.35	12.92 „	3.35	12.75 »

The results of these experiments are more intelligible when represented in the following way:

First bough experimented on.

	Length of period	Total transpiration	Average transpiration in 5 minutes
9.25 till 9.45	20 minutes	300 milligrm.	75 milligrm.
9.45 „ 10.10	25 „	200 „	40 „
10.10 „ 10.45	35 „	300 „	43 „
10.45 „ 11.15	30 „	430 „	72 „
11.15 „ 11.45	30 „	450 „	75 „
11.45 „ 2.	135 „	1520 „	56 „
2. „ 3.35	95 „	1100 „	58 „

Second bough experimented on.

	Length of period	Total transpiration	Average transpiration in 5 minutes
9.35 till 10.	25 minutes	200 milligrams	40 milligrams
10. „ 10.15	15 "	150 "	50 "
10.15 „ 10.55	40 "	400 "	50 "
10.55 „ 11.25	30 "	430 "	72 "
11.25 „ 11.55	30 "	450 "	75 "
11.55 „ 2.15	140 "	900 "	32 "
2.15 „ 3.35	80 "	300 "	19 "

Third bough experimented on.

	Length of period	Total transpiration	Average transpiration in 5 minutes
9.40 till 10.	20 minutes	50 milligrams	12.5 milligrams
10. „ 10.20	20 "	80 "	20 "
10.20 „ 10.55	35 "	180 "	26 "
10.55 „ 11.25	30 "	300 "	50 "
11.25 „ 12.	35 "	410 "	59 "
12. „ 2.15	135 "	1380 "	51 "
2.15 „ 3.35	80 "	400 "	25 "

The three boughs were cut off at the same time, about 9.20; the weighing of the first bough took place therefore about five minutes, that of the other two fifteen and twenty minutes after cutting. Whether the transpiration in the interval between cutting off and the first weighing changed noticeably, cannot be ascertained, but what is important is that the behaviour of the three boughs agrees, for they all, $^3/_4$—1 hour after the cutting (when they had lost from $1^0/_0$ to $4^0/_0$ of their weight by transpiration) show a distinct rise in the intensity of transpiration, which about two hours later (when the loss by transpiration of the boughs had risen to from 6 to 10% of their original weight) reached a maximum and then declined again.

Boughs of *Pirus malus* and *Populus nigra* which were investigated in the same way at the same time as those of *Viscum* showed no similar phenomena; the intensity of transpiration was here very great and remained almost unchanged until the boughs had dried up. In an experiment conducted some days later in precisely the same way with some evergreens (*Hedera helix, Pinus spec, Abies spec.* etc.) transpiration was at first also great, but gradually declined until a minimum was reached. Therefore these evergreens showed nothing of the irregularity which was noticed in *Viscum.*

The ready conclusion that in the experiment with *Viscum* it was not a question of one or another disturbing factor, which had been overlooked, but probably of some physiological peculiarity due to the structure of the stomata, was further confirmed by the fact that on looking through the protocols of my experiments I found again very clearly the same irregularity in an experiment conducted in Brazil with *Rhipsalis Cassytha.* The structure of the stomata of this plant agrees in several very obvious characteristics with those of *Viscum album.*

For the experiment, of which I give here the results only so far as they bear upon the phenomenon in question, a large plant was carefully loosened from the tree on which it grew, and hung up in the laboratory. The weight of this plant was recorded at intervals for a period of 136 days.

The following diminution in weight was observed:

during	the	first	24 hours		1,36 %	of the original weight
,,	,,	second	,,		2,10 %	
,,	,,	third	,,		2,13 %	
,,	,,	fourth	,,		1,77 %	
,,	,,	5th, 6th and 7th	,,	on the average	0,94 %	
,,	,,	8th and 9th	,,	,, ,, ,,	0,904%	
,,	,,	10th and 11th	,,	,, ,, ,,	0,86 %	
,,	,,	12th to 16th inclusive	,,	,, ,, ,,	1,01 %	
,,	,,	17th ,, 28th ,,	,,	,, ,, ,,	0,88 %	
,,	,,	29th ,, 37th ,,	,,	,, ,, ,,	0,68 %	
,,	,,	38th ,, 76th ,,	,,	,, ,, ,,	0,42 %	
,	,,	77th ,, 104th ,,	,,	,, ,, ,,	0,23 %	
,,	,,	105th ,, 136th ,,	,,	,, ,, ,,	0,15 %	

We see here also how the intensity of transpiration increases when the plant investigated has lost ± $1^1/_2$ % of its weight and then later decreases (when the loss by transpiration has risen to ± 6 %). Simultaneously with this experiment on *Rhipsalis Cassytha* some other plants (*Pothos aurea*, *Philodendron* spec., *Aechmea* spec., *Vriesea* spec. div.) were investigated by the same method, without showing this peculiar irregularity in the transpiration.

It may clearly be assumed that in the case of *Viscum album* and *Rhipsalis Cassytha* we have to deal with the antagonism between the guard-cells of the stomata and the adjacent epidermal cells, which has been often mentioned in the literature, but nevertheless remains the subject of controversy. The epidermal cells next to the stomata are in both plants differentiated from the other epidermal cells, and are developed as so-called subsidiary cells of the stoma

As my considerations and conclusions are limited to the plants investigated, it would lead us too far afield to quote the whole literature of the mechanism of the stomata; it will be enough to characterise the current view of the antagonism between the guard-cells and the adjacent epidermal cells.

Mohl and Leitgeb have assumed, partly on the evidence of experiments with isolated pieces of epidermis, that the stomata are passively closed through the turgor of the adjacent epidermal-cells.

Schwendener and his school on the other hand defended the view that the subsidiary cells are of little or no importance for the stomatal mechanism.

Pfeffer [1]) in 1897 in a survey of these views pointed out that the results of these various investigators only differed quantitatively and that in experiments with isolated pieces of epidermis the different rate of water-absorption in the various cells may have a great influence on the phenomena which are observed in the stoma.

Benecke [2]) in 1892 published a special study of the subsidiary cells of the stomata, and came to the conclusion that the subsidiary cells have in Succulents the function of eliminating the influence on the stomata of pressure and tension, which in consequence of the crumpling of the leaves through loss of water, are set up in the epidermis.

Benecke scarcely touches on the question of the antagonism between guard-cells and subsidiary cells: "Wir verfolgen diese Streitfrage "über die Bedeutung der Nebenzellen hier nicht weiter sondern

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[1]) Pfeffer, Pflanzenphysiologie. Zweite Auflage 1897, Erster Band, S. 173.

[2]) Benecke, Die Nebenzellen der Spaltöffnungen, Botanische Zeitung 1892.

"präcisiren nur noch unsere Stellungsnahme zu derselben. Es sei "betont dass wir eine allgemein gültige Lösung dieser Frage hier "nicht geben wollen noch können. Unserer Ansicht nach ist eben "die Fragestellung nach der Rolle der Nebenzellen in dieser Allgemeinheit unrichtig, weil höchst wahrscheinlich diese eine von Fall "zu Fall wechselnde ist. Im Allgemeinen richtig wird eine vermittelnde Stellungsnahme sein: Die Oeffnung des Spaltes wird durch "der Turgor der Schliesszellen selbst bewirkt, die angrenzenden Epidermiszellen müssen in vielen Fällen zum Verschluss mit beitragen."

In 1899 Westermaier [1]) published an investigation on stomata and their accessory apparatus in which he does not deal at all with the question of the antagonism between guard-cells and adjacent epidermal cells.

In 1902 Copeland [2]) published a detailed inquiry into the mechanism of the stomata in which he takes the view that the turgor of the adjacent epidermal cells can only play a passive part in bringing about the movement of the stomata. "In stomata, whose outline changes "with their movements, and only in these, the turgescence of the "contiguous cells must be a factor in determining the state of equilibrium, "open, closed, or intermediate. But because the pore closes with excessive "transpiration when turgescence in the leaf is least, because the "contents of the guard-cells furnish a clue to changes in turgor "which is wanting in the neighbouring cells, because some stomata "do not change their outline (surface view) in their movements, "because isolated stomata usually move like those on uninjured "leaves, and because the forms and structures of the guard-cells are "explicable and intelligible on this ground only, the conclusion cannot "be escaped that the turgescence of the neighbouring cells is a "passive factor, the active one being, as Schwendener and his students "have maintained, the turgescence of the guard-cells".

Haberlandt [3]) in the last edition of his handbook hardly says anything about this question, but also clearly ascribes very little importance to the turgor of the adjacent cells. The only reference to the antagonism between the guard-cells and the epidermal cells is as follows: "Bei einigen Gräsern (Cynosurus echinatus, Aira capillita, "Briza maxima) ist die Zentralspalte auch im turgorlosen Zustande "der Schliesszellen, nach Tötung dieser, offen. In diesen Fällen müssen also, sofern die Spaltöffnungen überhaupt noch funktionsfähig

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[1]) Westermaier, Ueber Spaltöffnungen und ihre Nebenapparate. Festschrift für Schwendener. Berlin 1899.

[2]) Copeland, The Mechanism of Stomata. Annals of Botany XVI 1902.

[3]) Haberlandt. Physiologische Pflanzenanatomie. Dritte Auflage 1904.

"sind, die beiden seitlich gelagerten Nebenzellen durch ihren Turgor-"druck den Spaltenverschluss herbeiführen".

Jost [1] in a very recent handbook deals with the question in the following way: "Die Öffnungsweite der Spalte hängt übrigens "nicht allein von dem Turgordruck der Schliesszellen ab sondern "auch von dem Gegendruck der Nachbarzellen; wird dieser etwa "durch Anstecken der Zellen aufgehoben, so sieht man sofort "eine starke Spaltenöffnung in den Schliesszellen eintreten, ohne "dass in *diesen* der Druck gestiegen wäre. Umgekehrt kann aber "auch eine Druckzunahme in den Nachbarzellen einen passiven "Verschluss der Spaltöffnung herbeiführen. In wie weit indess die "Einwirkung der Nachbarzellen *in der Natur* eine Rolle spielt, dar-"über gehen die Meinungen der Autoren noch weit auseinander; "Schwendener [2] schreibt den Nebenzellen gar keine, Leitgeb [3] eine "sehr grosse Wichtigkeit zu, Darwin [4] vermittelt".

It seems to me that the peculiar irregularity in the regulation of evaporation in *Viscum album* and *Rhipsalis Cassytha* may be simply and naturally explained by assuming that when these plants begin to wither the pore of the stoma first widens under the influence of the antagonism of the guard-cells and subsidiary cells and is subsequently constricted.

The stomata of *Viscum album* are rather large and transverse to the long axis of the stem and leaves. In order to survey the complicated structure it is necessary to consider sections which have been cut from the apparatus in different directions and at different levels.

A section which divides the stoma into two halves in a direction perpendicular to the slit gives a view as represented in Fig. 4. The thickened ventral side of the epidermal-cells is seen, the thick ridges which surround the outer porch ("Vorhof") of the stoma, the subsidiary cells which to some extent surround the guard-cells above and below, and the very thick collenchymatous ridge which surrounds the inner cavity of the stoma. When a section of the stoma is made in the same direction, not however through the middle, but close to one of the extremities, the figure is different.

The lumen of the guard-cells is then (Fig. 5) seen to continue upwards in the shape of a wedge. The dividing-wall between the subsidiary cell and this wedge-shaped continuation of the guard-cell is thickened. In the diagrammatic Fig. 1, the lines *a*, *b*, and *c*

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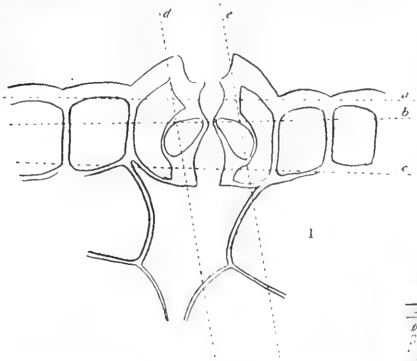
[1] Jost. Pflanzenphysiologie. Dritte Auflage 1913. Seite 58.

[2] Schwendener 1881. Monatsberichte Berliner Akademie. S. 833.

[3] Leitgeb 1886. Mittheilungen aus dem botanischen Institut zu Graz I.

[4] Darwin 1898. Philos. Transactions (B) 190.

Z. Kamerling, ON THE REGULATION OF THE TRANSPIRATION OF VISCUM ALBUM AND RHIPSALIS CASSYTHA.



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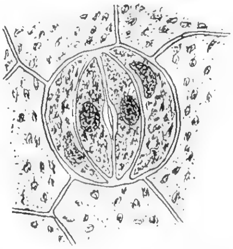

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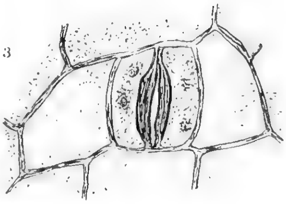

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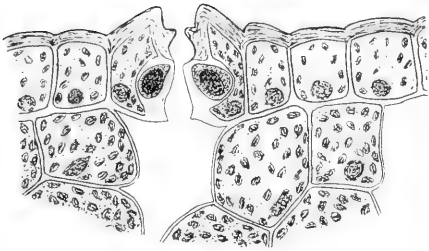

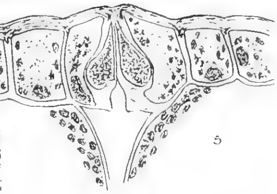

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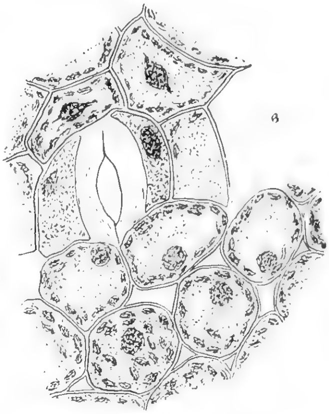

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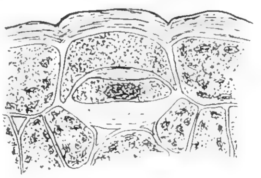

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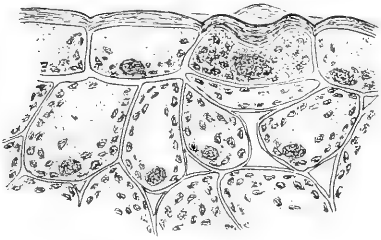

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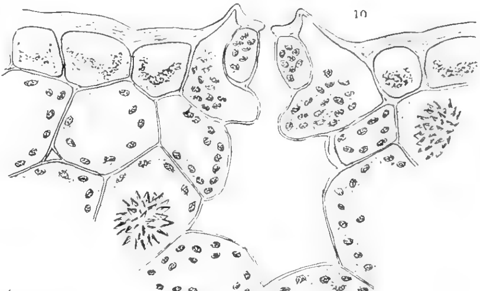

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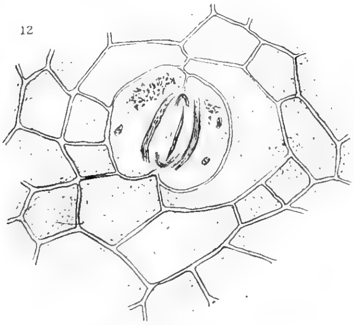

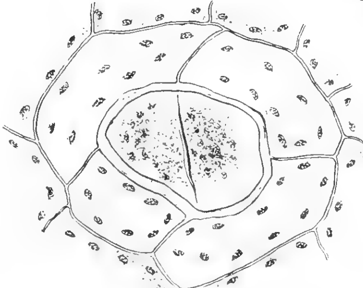

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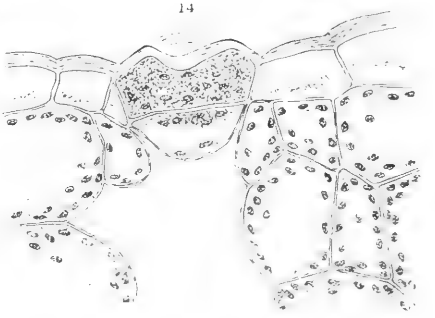
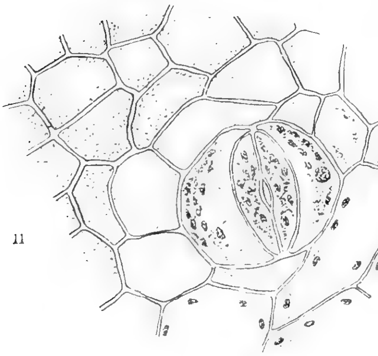
9c

14





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9b

indicate three possible levels at which the stoma may be cut in sections parallel to the surface; the lines *d* and *e* indicate two possible ways in which in a transverse section through the leaf a razor directed more or less parallel to the slit opening of the stoma, may hit the different parts.

In sections roughly corresponding to line *a*, the slit of the "Vorhof" (Fig. 3) is seen to be bounded by two strong, very much cuticularized ridges which continue on both sides as a non-cuticularized strip united to the cell-wall of the adjacent epidermal-cells. The razor has now passed above the guard-cells without touching them; the cells seen in Fig. 3 on both sides of the opening, are the subsidiary cells. When such preparations are treated with iodine and zinc chloride, the distinction between the cuticularised ridge and the non-cuticularised strip into which the latter passes on both sides, becomes perfectly clear.

Such preparations suggest the comparison of the non-cuticularised strip to a ligament of articulation. Preparations of this nature, treated with iodine zinc chloride show that the guardcells of the stoma, wherever they border on the slit or on the respiratory cavity, are covered with a thin cuticle.

When a similar preparation, as is seen in Fig. 3, is treated with strong sulphuric acid, conditions such as those shown in Fig. 9 may result. The non-cuticularised "ligaments of articulation" are here dissolved; but the two cuticularised ridges which occur in their normal condition in *a* and *b* are still seen, but in *c* they are separated from one another and have fallen over outward. The thin cuticle which covers the inner side of the guard-cells adjoins these edges. The "ligaments of articulation" are simply the thickened strips of membrane which in Fig. 5 are shown in transverse section between the wedge-shaped continuation of the lumen of the guard cell and the subsidiary cell.

When in preparations parallel to the surface, the stoma is cut at a lower level corresponding roughly with the line *b* of Fig. 1, that is to say about in the plane of the "central slit" a view is obtained like that drawn in Fig. 2. The slit is here short and narrow, the inner wall of the guard-cell is clearly thickened where it adjoins the slit. The subsidiary-cells at this level surround the guard-cells like a crescent. A section at a lower level, roughly corresponding to line *c* of Fig 1, passes under the lumina of the guard-cells without touching them. It is then seen, as Fig. 6 represents, that the inner cavity of the stoma is surrounded by two thick ridges of cellulose. The cell-cavities which are seen on either side of these ridges are not those of the guard-cells but of the subsidiary cells.

When a transverse section through the leaf, somewhere about the line *d* of Fig. 1, cuts the stoma parallel to the long axis, a view is obtained corresponding with Fig. 7. From above downwards the much thickened and cuticularised outer-wall, the lumen of the subsidiary cell, the wall dividing the subsidiary cell from the guard-cell, the lumen of the latter and the thick ridge of cellulose here follow each other. If on the other hand the razor follows the line *e*, then as in Fig. 8, we see from above downwards the cuticularised edge which adjoins the "Vorhof", the lumen of the guard-cell, the wall separating the guard-cell from the subsidiary cell, and the lumen of the subsidiary cell. In similar longitudinal sections through the stoma, the subsidiary cell can be seen either above or below the guard-cell, according to the direction in which the section is made. In Fig. 8 we may see also the peculiar shape of the guard cell, somewhat like that of a dumb-bell, which can also be made out by combining the sections of Fig. 4 and Fig. 5.

If we now wish to get an understanding of the functions of this complicated apparatus, we must assume that the outer slit formed by the ridges of the cuticle can be considerably narrowed and widened. Perhaps the inner slit, bounded by the thick edges of cellulose can also be narrowed and widened, though in all probability only to a slight extent. Variations of turgor in the subsidiary cells, must, as is at once clear from the structure, exert an influence on the width of the outer slit.

The central slit (Centralspalte) is doubtless also capable of variation in width; it seems however that it is never wholly closed, but that a small opening always remains, as represented in Fig. 2.

As long as the subsidiary cells are turgid, they offer resistance to the pressure of the guard-cells; they cannot curve as strongly and open the central slit as widely as would be the case if no counter-pressure were exerted by the subsidiary cells.

When in consequence of transpiration, the turgor of the subsidiary cells decreases before that of the guard-cells, a stronger curvature of the latter and widening of the central slit must take place.

It is likely that, when the plant first withers, the turgor indeed decreases earlier in the subsidiary cells than in the guard-cells, because the guard-cells are almost completely surrounded by the subsidiary-cells and the small part of the wall of the guard-cells adjoining the opening is rather strongly cuticularised. I believe that in the first place the chlorophyll-containing parenchyma loses water by transpiration, that these cells abstract water from the epidermal-cells and from the subsidiary cells of the stomata, and that finally the subsidiary cells draw water from the guard-cells.

The characteristic peculiarity of the stomata in question seems to me to consist in: 1. That the guard-cells have only a small free surface, the wall of which is fairly strongly cuticularised and 2. that they adjoin no epidermal cells other than the subsidiary cells so that the influx and efflux of water in the guard-cells is brought about entirely through the medium of the subsidiary cells.

When indeed turgor decreases in the subsidiary cells before it does in the guard cells there must therefore, when the plant begins to wither, be a widening of the central slit of the stomata. In this first stage when turgor in the subsidiary cells is already diminished, but is still unchanged in the guard-cells, the subsidiary cells tend to constrict the outer slit, the guard-cells tend to widen it.

When, at a later stage, turgor has also decreased in the guard-cells, the subsidiary- and guard-cells cooperate to cause the outer slit to contract and then the central slit also contracts.

In my investigation of the structure of the stomata of *Rhipsalis Cassytha* I had only at my disposal material from a hot-house, since I had omitted to bring from Brazil spirit material of this plant.

The stomata are here, just as in *Loranthaceae* mostly arranged transversely to the long axis [1]) of the stem.

A median longitudinal section through the stem shows that, as in *Viscum album*, the subsidiary cells surround the guard-cells above and below. Fig. 10 represents such a section perpendicular to the direction of the slit and approximately through the middle of a stoma of *Rhipsalis Cassytha*.

In a transverse section through the stem, longitudinal sections of the stoma can be obtained as in Fig. 14 in which the bulging lower part of the subsidiary cell can be seen under the dumb-bell-shaped guard-cell and above the latter, in the background, the fold in the wall of the subsidiary cell, which fold can be recognised in Fig. 10 and projects above the level of the other epidermal cells.

A section which, parallel to the surface, passes through the plane of the outer slit above the guard-cells without touching them, is given in Fig. 12. The two folds of the cell-wall are seen and between them the narrow outer slit which is bounded at either end by a small curved fold which is not always equally distinct.

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[1]) This peculiar orientation is somewhat rare. Löw found it in *Casuarina*, Pfitzer, inter alia, in *Colletia*, the present writer observed it also in *Cassytha filiformis*.

The two large crescent-shaped cells which might at first sight be taken for the guard-cells, are in reality the subsidiary cells. When the stoma is similarly cut parallel to the surface but at a lower level, at about the depth of the central slit, it may be represented as in Fig. 11. The section was not completely parallel to the surface of the stem; on one side (the upper one in the figure) the ordinary epidermal cells are cut, on the other side (the lower one in the figure) the section passes through sub-epidermal cells.

If the stoma is cut at a still lower level, a view may be obtained as represented in Fig. 13. Those parts of the walls of the surrounding parenchymatosis cells which border on the internal air space are (generally though not always) somewhat considerably thickened[1]) and in the channel thus formed the two subsidiary cells are seen, separated by a long and very narrow slit. Fig. 13 was drawn from a preparation viewed from the inner side.

It appears that in the stomata of *Rhipsalis Cassytha* constriction and dilatation can take place in three places: 1. At the level of the central slit between the relatively thin parts of the wall of the two guard-cells, 2. at the level of the outer slit between the thick, strongly cuticularised edges which bound this outer slit on both sides, 3. in the plane beneath the guard-cells between the thin-walled parts of the subsidiary cells which bulge out downwards.

The assumption is obvious that in *Rhipsalis Cassytha* also, at the first withering of the plant, turgor decreases earlier in the subsidiary cells than in the guard-cells and that first, as in *Viscum album*, dilatation of the central slit and increased amount of transpiration per unit of time, results from this.

The characteristic peculiarity to which the observed irregularity in transpiration is due in both plants investigated, lies, I consider, principally in the manner in which each guard-cell is surrounded by an epidermal-cell which is developed as a subsidiary cell and separates the guard-cell from the other epidermal cells. It seems to me probable that in other plants also, whenever the stomata are constructed in a similar manner, this same irrigularily in the evaporation will be found. In *Loranthus dichrous* of Brazil this same peculiarity seems to occur, less clearly than in *Viscum album* and *Rhipsalis Cassytha*, but nevertheless in a very similar manner as the following figures show.

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[1]) This point was brought out by Vöchting, Beiträge zur Morphologie und Anatomie der Rhipsalideën Pringsheim's Jahrbücher IX. 1873—74.

Benecke and Westermaier (l. c.) also mention this peculiarity and state their theory of its probable significance.

Transpiration of two boughs of Loranthus dichrous Mart.
Exposed to the sun.

P. M.	First bough		Second bough	
	observed weight	loss of weight	observed weight	loss of weight
1.9	29.9 grammes		25.5 grammes	
1.14	29.1 „	0.8 gramme	24.9 „	0.6 gramme
1.19	28.4 „	0.7 „	24.5 „	0.4 „
1.24	27.8 „	0.6 „	24.05 „	0.45 „
1.29	27.0 „	0.8 „	23.6 „	0.45 „
1.34	26.5 „	0.5 „	23.1 „	0.5 „
1.39	26.05 „	0.45 „	22.75 „	0.35 „
2.9	23.5 „	0.41 gr.	20.7 „	0.34 gr.
2.39	20.8 „	0.45 „ average per five minutes	18.95 „	0.29 „ average per five minutes
3.9	18.3 „	0.42 „	17.0 „	0.325 „

These figures refer to a comparative experiment made in Campos on transpiration in *Loranthus dichrous* and *Psidium guajava*; regulation of transpiration took place regularly in the last species, but in *Loranthus dichrous* it took a noticeably irregular course. We see here also that at first the amount of transpiration per unit of time decreases, later distinctly increases (when the boughs have lost ± 5 °/₀ in weight) and finally diminishes again (when the loss in weight amounts to ± 10 °/₀). When the experiment was finished at 3.9 both boughs already began to dry.

The results of this investigation may be summarised as follows: When cut leafy boughs or whole plants are allowed to wither and the transpiration is followed by means of periodical weighings, it is found in most plants, either that the amount of transpiration per unit of time remains approximately constant until the bough is dried up or that these amounts decrease uniformly until the transpiration is reduced to a minimum.

In *Viscum album* and *Rhipsalis Cassytha* the peculiar phenomenon is observable when the same experiments are made, namely, that when the bough (or plant) under investigation has lost a certain proportion of its weight (varying from 1 °/₀ to 4 °/₀) the amount of transpiration per unit of time increases and then later, when the loss in weight has increased (varying from 6 to 10 °/₀), the transpiration decreases again.

We may assume that this increase in the intensity of transpiration when the plant first withers is caused by the dilatation of the openings of the stomata, a dilatation which is however only of comparatively short duration and is later again followed by constriction:

The dilatation of the stomata is probably caused by the antagonism between the guard-cells and the subsidiary cells of the stomata in such a way that turgor in the subsidiary cells begins to decrease sooner than in the guard-cells, this phenomenon causing a stronger curvature of the guard-cells and dilatation of the slit of the stomata.

The subsidiary cells of the stomata, in *Viscum album* as in *Rhipsalis Cassytha*, surround the guard-cells in a peculiar manner; probably it is in this fact that the cause must be sought for the irregularity of transpiration, with which this paper is concerned.

EXPLANATION OF THE FIGURES.

All drawings, except the diagrammatic figure 1 and figure 9, relating to a preparation treated with concentrated sulphuric acid, were made from unstained preparations of spirit material, cut by hand and treated in the usual way. The drawings were made by means of a camera lucida.

Fig. 1. Diagrammatic transverse section of a stoma of Viscum album. The lines *a*, *b*. *c*, *d*, an *e* give the various directions and levels at which the stoma was cut, line *a* corresponds roughly with Fig. 3, *b* with Fig. 2, *c* with Fig. 6, *d* with Fig. 7, *e* with Fig. 8.

Fig. 2. Viscum album. From a section parallel to the surface of the leaf. The level is roughly that of line *b* in Fig. 1.

Fig. 3. Viscum album. From a section parallel to the surface of the leaf. The level is roughly that of line *a* in Fig. 1.

Fig. 4. Viscum album. From a longitudinal section through the leaf. The stoma in transverse section, the guard-cells roughly halved.

Fig. 5. Viscum album. From a longitudinal section through the leaf. Stoma cut transversely, close to the extremity.

Fig. 6. Viscum album. From a section parallel to the surface of the leaf. Level about that of line *c* in Fig. 1.

Fig 7. Viscum album. From a transverse section through the leaf. The stoma is cut parallel to the slit, roughly in the direction of the line *d* in Fig. 1.

Fig. 8. Visum album. From a transverse section of the leaf. The stoma is cut parallel to the slit, in the direction roughly of line *e* in Fig. 1. The preparation was in such a position that the opening of the stoma removed by the razor, would have been found on the upper edge.

Fig. 9. Visum album. From a section parallel to the surface, treated with sulphuric acid. The cuticular ridges which are seen in Fig. 8 in relation to the cell-wall net, have been loosened by the action of the sulphuric acid. The "ligaments of articulation" are dissolved in the sulphuric acid; *a* and *b* are in normal position, at *c* the ridges have fallen outwards.

Fig. 10. Rhipsalis Cassytha. From a median longitudinal section through the stem. The stoma in transverse section, the guardcells roughly halved. The section has been somewhat distorted in cutting and preparing, so that the slit, especially in the middle and below, is wider than in the intact plant.

Fig. 11. Rhipsalis Cassytha. From a section parallel to the surface. The level is that of the central slit.

Fig. 12. Rhipsalis Cassytha. From a section parallel to the surface. The level is above the guard-cells, the outer slit is seen.

Fig. 13. Rhipsalis Cassytha. From a section parallel to the surface, placed in an inverted position on the slide. The level is below the guard-cells, the canal-shaped internal air space is seen, which is closed by the two subsidiary cells.

Fig. 14. Rhipsalis Cassytha. From a transverse section through the stem. The stoma in longitudinal section parallel to the slit, in a direction roughly corresponding to line *e* in Fig. 1, the preparation is orientated in a corresponding manner to the preparation of Viscum drawn in Fig. 8.

Leiden, December 1913. *Botanical Laboratory.*

Botany. — "*The explanation of an apparent exception to* MENDEL's *law of segregation.*" By Miss TINE TAMMES. (Communicated by Prof. J. W. MOLL).

(Communicated in the meeting of February 28, 1914).

In experiments on hybridisation in recent years various cases have been observed in which the numerical proportion of different forms occurring in the second generation does not agree with what might be expected according to MENDEL's law. Among these there are very many with respect to which there is no reason to assume that this law does not apply, and in the greater number of these cases it has been possible to show the causes of the discrepancy. These causes have been found to be of two kinds. Firstly, there may be deviations which are only the results of mistakes or wrong hypotheses on the part of the observer. Secondly, there are cases in which the deviations are due to the plant itself. The sources of error belonging to the first class are chiefly as follows.

1. It may happen that the deviation is the result of making too few observations.

2. The observer may have wrongly estimated the difference in the number of factors of the *P*-forms, so that the numerical proportion he expects, is wrong.

3. Characters have to be dealt with, which cannot be seen at the same moment in different individuals. If the observations in such a case are extended over too short a period of time, then wrong results are obtained.

4. In consequence of a strongly fluctuating variability of characters the observer has failed to distinguish the different genotypes with sufficient sharpness.

The known cases in which the cause of the deviation lies in the plant itself, are the following.

1. There are fewer gametes of a particular kind formed than ought to arise. The deviation then already arises in the formation of the sexual-products.

2. The union of some kinds of gametes comes about with more difficulty than that of others. The deviation then lies in the fertilisation-process.

3. Certain combinations of gametes are less capable of life than others, so that the young individuals die off before the character can be observed.

4. The different genes may be coupled or may repel one another.

Of all the various phenomena here enumerated examples are known. BAUR [1]) and especially PLATE [2]) give a survey of them in their textbooks.

The case, which I wish to deal with here, belongs to the second group, in which the cause of the deviation lies in the plant itself. The nature of this cause will be made clear below.

The phenomenon appeared on the crossing of a white- and a blue-flowering variety of *Linum usitatissimum* and related to the colour of the flower. The blue-flowering form was a variety obtained from Egypt, and has been described by me [3]) previously and named Egyptian flax. The seed of the variety with white flowers was obtained from Messrs. VILMORIN-ANDRIEUX of Paris. Pure lines of both varieties were used for the investigation and the reciprocal crossings were carried out in 1908 and in 1911. The whole number

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[1]) E. BAUR, Vererbungslehre. 1911, p. 116.

[2]) L. PLATE, Vererbungslehre. 1913, p. 194.

[3]) Der Flachsstengel, eine statistisch anatomische Monographie. Verh. v. d. Holl Maatsch. d. Wetensch. Haarlem, Verz. 3, Deel VI, Stuk 4, 1907, p. 22.

Das Verhalten fluktuierend variierender Merkmale bei der Bastardierung. Rec. d. Trav. bot. Néerl. Vol. 8, 1911, p. 206.

of crossings amounted to 20; the first generation consisted of 30 plants, which all had blue flowers. In different years further cultures of the 2nd, 3rd ,and 4th generation were grown. The following table gives a survey of the observations on both reciprocal crossings, since the two sets agree. Circumstances prevented the second generation from being cultivated in 1910; it was obtained for the first time in 1911.

	White	Blue	Ratio per 4 indiv.	Deviation
F_2 1911	134	482	0.871 : 3.129	∓ 0.129
„ 1912	146	481	0.931 : 3.069	∓ 0.069
„ 1913	18	87	0.686 : 3.314	∓ 0.314
„ „	69	291	0.767 : 3.233	∓ 0.233
„ „	9	39	0.750 : 3.250	∓ 0.250
„ „	14	44	0.966 : 3.034	∓ 0.034
„ „	34	130	0.829 : 3.171	∓ 0.171
F_3 1912	113	493	0.745 : 3.255	∓ 0.255
„ 1913	91	311	0.905 : 3.095	∓ 0.095
F_4 1913	172	748	0.748 : 3.252	∓ 0.252
Total	800	3106	0.819 : 3.181	∓ 0.181

In the second and third vertical column the number of white- and of blue-flowering plants in each culture is given. It is seen from this, that the proportion of these two deviates more or less from the ratio 1 : 3. In order to make clear the extent of the deviation the ratio for each culture is reckoned per four individuals. The figures obtained are given in the fourth column and in that following it the deviations of these from the theoretical ratio 1 : 3.

In the second place, the table shows that the deviation in all cases is in the same direction. The number of white-flowering plants is always less than was to be expected, or as we may also consider it, the number of blue-flowering ones is greater. Since here however the former case obtains, as will be shown later, I shall indicate the deviation in future as a deficiency of white-flowering plants. Further it is seen from the table that the deviations, with the exception of one small culture, are considerable. For the whole number of observations on 800 white and 3106 blue ones the deviation calculated for these figures amounts to ∓ 0.181. The mean error for this number is 0.027; the deviation is therefore about 6.5 times greater. This shows that the deviation from the ratio cannot be ascribed to chance, but that a definite cause must exist. The question is now what this cause is. Of the four causes mentioned above, which result from errors or wrong suppositions, three do not here come into consideration. With regard to the first, the number of observations is very great, with regard to the second the flowering of all of the plants was observed and with regard to the third cause fluctuating variability plays no role here. The only remaining cause therefore is a wrong hypothesis as to the number of factors in which the P-forms differ. For it is possible that the numerical ratio to be expected is not 1 : 3, and that therefore we have not to deal with a monohybrid crossing or with a polyhybrid behaving as a monohybrid, but that here several factors occur, which cause the blue colour of the flower. The number of gametes in which the factors for blue are wholly absent will then be relatively smaller and white-flowering plants will arise in the second generation in smaller proportion than in monohybrid crossing. In the case in which the number of factors for blue amounts to two, each by itself producing the colour, the proportion of white and blue in F_2 is 1 : 15, whilst with three factors for blue the proportion is already 1 : 63. These proportions differ so much from the observed ones, that the cause must be different. Also when it is assumed that the blue colour is caused by still more factors, which separately or in definite groups can produce this colour, ratios are obtained which do not in the least agree with that which was observed. If indeed the existence is assumed of a very great number of factors which only produce blue when combined in a certain way, a ratio may be arrived at which sufficiently agrees with the given one. Such an assumption would only have a reasonable basis, when the phenomenon could not at all be explained in an other way. I have found, however, that we are not dealing here with complicated relations of factors, but that there are two other causes, which together produce the deficiency of white-flowering plants.

The first concerns the germinating-power of the seed.

I have repeatedly noticed that the seed of white-flowering varieties has a germinating-power inferior to that of the blue ones, i.e. a relatively smaller number of seeds of the former germinate. This difference existed also between the two forms which I crossed. The seed of Egyptian blue flax, which I used for my cultures, had very good power of germination; almost all its seed came up, as the following figures show. Out of 706 seeds 701 germinated and developed to plants, thus only 0.71 °/₀ failed. The white-flowering flax, on the other hand, germinated badly and a number of seedlings died at a very early stage. 682 seeds yielded 601 plants, that is a loss of 11.9 °/₀. Now there are obtained from the F_1 plants and the heterozygous plants of the following generation both seeds producing white-flowering plants and seeds producing blue ones. If then a higher percentage of this seed than of the blue flax does not germinate, then it may safely be assumed that the loss almost entirely arises through the failure of the seeds of the white-flowering plants. I have not traced the proportion between the number of seeds sown and the number of plants obtained for all the cultures of the whole 3906 plants to be found in the table, but only for about the half. From these it was found that 1916 seeds yielded 1858 plants. There was therefore for 1858 plants obtained a loss of 58. That will amount to 122 for the 3906 plants reckoning all the cultures together. Since of the 3906 plants 3106 had blue flowers and since we saw that among the blue P-form the 701 plants obtained, 5 seeds did not germinate, we may assume that in this case out of the 122 seeds which did not germinate, there were 22 which should have given blue-flowering plants and consequently 100 which should have given the white-flowering ones. In this it is assumed that heterozygotes behave as homozygous blues. I shall return to this point later.

Now we may inquire whether the number of 100 thus found is sufficient to explain the whole deficiency of white-flowering plants. 3106 blue-flowering plants were observed, to which belong 22 seeds which did not germinate. We may therefore assume, that among the seeds which were sown, there were 3128 of them with a predisposition towards the blue colour of the flower. Theoretically $^1/_3$ of this number, that is $1042\,^2/_3$, or in round number 1043 seeds should have given white-flowering plants.

Only 800 are found, however. The deficiency amounts therefore to 243. Now we saw that by reason of the inferior germinating-power of the seed 100 white-flowering plants will be wanting. This is, however, much less than the observed deficiency, so much less that the aberrant ratio of the number cannot be explained by this means alone; some other cause must also be present which acts in the same direction.

I have indeed succeeded in demonstrating this second cause of the deficiency of white-flowering plants. It is connected with the average number of seeds which are formed in the fruit of flax. The flax-fruit may contain a maximum of ten seeds. The average number, however is distinctly less, and in the white variety it is, as I repeatedly observed, in general still smaller than in the blue one.

Now when the average number of seeds in the fruits of the heterozygotes, which contain both seeds of white- and of blue-flowering plants, is smaller than in the blue *P*-form, then the assumption is plausible, that this is caused, by the formation of relatively fewer seeds of white-flowering plants. If this seed is sown a progeny arises with a deficiency of white-flowering plants.

The investigation was however not so simple in this case. In contradistinction to the foregoing it was found that in the crossed varieties the fruits of the white flax had on the average even a greater number of seeds than those of the blue Egyptian flax. In 330 fruits of the white flax the number of seeds amounted to 2412, an average of 7.31, while in 219 fruits of the Egyptian flax, there were 824 seeds, an average of 3.76. In the white variety the average number of seeds, is therefore almost twice as great as in the blue.

Now the seed of Egyptian flax is, however, much larger than that of the white flax and comparisons of different varieties had already convinced me before that the average number of seeds is closely connected with the size of the seed and in such a way that in varieties with large seeds the average number is in general smaller than in varieties with small seeds. It is therefore possible, that in the white flax there is indeed a tendency to produce a smaller number of seeds than the average number of the Egyptian flax, but that this tendency is not revealed at all, because the difference in size of the seed of the two varieties is accompanied by a much greater difference in number in the opposite direction. In order to make this out it is necessary therefore to eliminate the influence of size. This is indeed possible in the case under consideration. My earlier investigations¹) have shown that the difference in size between the seed of Egyptian flax and that of *Linum angustifolium* is caused by several factors. Consequently there arise in the second generation forms differing in the size of the seed, intermediate between that of

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¹) Das Verhalten fluktuierend variierender Merkmale bei der Bastardierung. Rec. d. Trav. bot. Néerl. Vol. 8, 1911, p. 212.

the two *P*-forms. The majority however of the F_2 plants show the mean type. This also holds for the crossing of Egyptian with white-flowering flax. Here also F_2 shows, so far as size of seed is concerned, a continuous series of forms in which the mean is most strongly represented. It was therefore not difficult to find in F_2 and F_3 a certain number of plants which agreed in size of seed. Among these were blue-flowering ones which from investigation of their progeny were found to be homozygous for the colour of the flower and in this therefore were equal to the blue *P*-forms. At the same time there were also white-flowering plants in this lot. These are always homozygous and did not therefore require to be cultivated further. Now since the size of the seed in these forms was the same, they could independently of this point be compared as to their average number of seeds.

An investigation of these plants gave the following results. 1100 fruits from 94 homozygous blue-flowering plants of F_2 and F_3 were examined. These yielded 6468 seeds, an average of 5.88. 71 white-flowering plants from F_2 and F_3 yielded in 800 fruits 4112 seeds, an average of 5.14. These two mean values are intermediate between those of the *P*-forms, in connection with the size of the seed which is also intermediate. But it further results that the white-flowering plants have a smaller number of seeds in the fruits than the blue-flowering ones, namely as $12.6^0/_0$ less than the blue ones. This difference cannot, when the large number of the observations is taken into account, be ascribed to chance.

A second cause of the aberrant numerical proportion is in this way demonstrated. The question now remains to what extent the deficiency in white-flowering plants can be explained by this means.

As stated above, out of the whole number of cultures 1043 white-flowering plants might be expected theoretically. The difference in the average number of seeds formed between the white and the blue varieties amounted to $12.6^0/_0$, i.e., for every 100 seeds of white-flowering plants 12.6 will be wanting. For 1043 seeds this would amount to $10.43 \times 12.6 = 131$, from which a corresponding deficiency in white-flowering plants will arise.

By reason of both these causes together a deficiency of $100 + 131 = 231$ white-flowering plants can be explained. The deficiency actually amounts to 243 plants. The difference between these two values is insignificant. It may therefore be considered proved that the lesser germinating-power and the lesser number of seeds per fruit of the white-flowering variety are the causes of the aberrant numerical proportion. Although the deficiency is not wholly accounted for by the two causes, yet I do not believe that it is necessary to postulate a third cause for the absence of white-flowering plants.

In the foregoing it has been assumed in all calculations that the heterozygous blues behave as homozygous. I came to this conclusion because of an investigation of the progeny of blue-flowering F_2 individuals. Normally $^1/_3$ of the blue-flowering F_2 plants are homozygous and $^2/_3$ heterozygous. If, however, heterozygotism were to exercise an influence, it would be noticeable in the number of seeds and in their germinating-power. In proportion to the seeds which are homozygous blue for the colour of flower there should be from hybrid plants a smaller number of heterozygotes formed and this seed should moreover have less germinating-power. The result would be that in the succeeding generation too few heterozygous blue-flowering plants occurred, which would be evident from the investigation of the progeny.

This inquiry now showed that out of 43 F_2 plants, 13 were homozygous and 30 heterozygous. Instead of a deficiency in heterozygotes this number is even greater than it should be theoretically. Although the figures are small, nevertheless I think that it may be concluded, that the heterozygous blue plants behave in the same way as homozygous ones.

As well as in the crossing between the blue Egyptian flax and the white flax described above, I observed similar aberrant numerical proportion in some other crossings between white- and blue-flowering varieties. In the crossing between VILMORIN's white flax mentioned above and the blue flax commonly cultivated in Holland 318 white-flowering and 1312 blue-flowering plants were obtained in F_2, that is in the proportion 0.78 : 3.22. The deviation here observed, ∓ 0.22 is even slightly greater than that found in the previous crossing. The deviation here must also consist in a deficiency of white-flowering plants, brought about by the causes mentioned above. This is clear from the following. In 211 fruits of the common blue flax the number of seeds amounted to 1851, an average of 8.78; whilst the average for the white flax was seen to be 7.31. The blue flax has therefore a higher average number of seeds in the fruit. These two values are directly comparable because the size of the seed is about the same. In connection with this, the average number of seeds in the fruits of F_1 lies between these two values and amounts to 8.38. In these fruits therefore, in proportion a somewhat smaller number of seeds is produced for white-flowering plants than for blue-flowering ones. The germinating-power also shows a difference capable of explaining a deficiency in white-flowering plants, because the common blue flax that was used in my experiments, germinates very well. Less than 1 °/₀ fails, as in the blue Egyptian flax, whilst the white flax, as has been said, shows a loss of 11,9 °/₀.

Besides the white flax from the firm of VILMORIN still another white variety was crossed with the two blue forms mentioned. This was cultivated as a pure line from a white-flowering form grown in the province of Friesland.

By crossing this white with the blue Egyptian flax there were obtained in F_2 60 white-flowering and 214 blue-flowering plants, that is in the proportion of 0.876 : 3.124 with a deviation of $\mp$ 0.124.

The crossing between the last mentioned white flax and the common blue one gave 30 white- and 104 blue-flowering individuals, a proportion of 0.895 : 3.105 with a deviation of $\mp$ 0.105.

In both cases a deficiency in white-flowering plants appeared in F_2. Although the number of observations is not great, I think it may nevertheless be concluded that we are here dealing with the same phenomenon, because in comparison with the blue-flowering varieties this white form also has a lower average number of seeds and an inferior germinating-power. The differences are however not so great as with the white flax obtained from VILMORIN.

The question now arises how the lesser number of seeds and the lesser germinating-power of the seeds of the white-flowering variety are caused. With respect to the number of seeds it is possible that the cause lies in the number of gametes formed. Normally in F_1 as many gametes without the factor for blue should be formed as those possessing this factor. Should there however be fewer gametes formed in which the factor for blue is absent, then there will be after fertilisation not only a relatively smaller number of homozygous whites but also fewer heterozygous ones and F_2 will necessarily have a deficiency in heterozygous blues as well as in whites.

As I have shown, this is not the case, there is here no deficiency in heterozygous plants. Therefore the cause does not lie in a differing number of the two kinds of gametes and can only be sought in phenomena at or after fertilisation. It may be that the union of two gametes, both devoid of the factor for blue, happens less easily so that in some cases no fertilisation takes place. Or it is also possible that the two gametes do unite and that a zygote is produced, but that the embryo already dies off in the first stages. In both cases there will be a deficiency of seed for white-flowering plants. Something of this kind was observed by CORRENS [1]) on crossing a black sugar maize *Zea Mais* var. *coeruleodulcis* KcKE. and a common white maize "Popcorn", *Zea Mais* var. *leucoceras* ALEF. Here a deficiency of sacchariferous granules occurred. CORRENS showed by crossing the F_1-hybrid again with the sugar-containing P-form, that the formation of an unequal number of the different gametes was not the cause of the phenomenon. He comes therefore to the conclusion that the deficiency arises because the gametes-combination of two sacchariferous ones happens less easily.

By crossing the varieties of flax a further deficiency was caused through the seed of the white forms having less germinating-power. It either does not germinate at all, the embryo has then already died in the seed, or the seedlings die off early. The latter agrees with the case observed by BAUR [2]) in cultivating the aurea-variety of *Antirrhinum majus*. From this form, which is heterozygous, there are produced green- and aurea-plants in the proportion of 1 : 2, because the yellow individuals formed at the same time die off very young.

It is clear from the inferior germinating-power of the seed of the white varieties of flax that the gametes-combination of white with white has less vitality. This suggests that very probably the smaller number of seeds is also wholly or partly to be ascribed to the same cause. I have not been able to ascertain whether seed is wanting because fertilisation does not take place at all. It can however be said in general, that the two phenomena, the smaller number of seeds and their inferior germinating-power, which in the foregoing have been always considered separately, are only the result of a single cause, namely the smaller vitality of the gametes-combination of white with white. Only because the death of certain individuals as a result of this cause may take place at different stages of development, two different phenomena can be observed separately.

I will finally add a few words on a point resulting from these observations. It is found that the number of seeds and their germinating-power, therefore the vitality of the gametes-combination, is connected with the colour of the flowers produced from such seed, that is with the presence or absence of the factor for that colour.

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[1]) C. CORRENS, Scheinbare Ausnahmen von der MENDEL'schen Spaltungsregel für Bastarde. Ber. d. d. bot. Ges. Bd. XX, 1902, p. 159.

[2]) E. BAUR, Untersuchungen über die Erblichkeitsverhältnisse einer nur in Bastardform lebensfähigen Sippe von *Antirrhinum majus*. Ber. d. d. bot. Ges. Bd. 25, 1907, p. 442.

The presence or absence of this factor is even more intimately connected with the number of the seeds and their germinating-power than the nature of the mother-plant which produces the seeds. For seeds with the colour-factor and seeds without it are formed in F_1 by the same plant, even in the same fruit and yet the number and the germinating-power of those without the colour-factor is less. We see therefore that the difference between the white and blue varieties of flax, so far as concerns the number of seeds and their germinating-power, is unconnected with the difference in nutritional relationships between the plants, but only with the presence or absence in the gametes of a factor for the colour of the flower.

The following is a summary of results.

In crossing white- and blue-flowering varieties of *Linum usitatissimum* there are formed in the second and following generations white and blue individuals in numerical proportions which are not in agreement with those to be expected in accordance with MENDEL's law of segregation.

In all cases there is according to the proportion 1 : 3 a deficiency in white-flowering plants.

The deficiency arises from two causes which act in the same direction: 1. By F_2 and by the heterozygotes of the following generation there is formed a relatively too small number of seeds which will yield white-flowering plants. 2. The germinating-power of the seed, that yields white-flowering plants is less than that of the seed which produces blue-flowering ones. The smaller number of seeds which yield white-flowering plants and the inferior germinating-power of these seeds are both the result of the lower vitality of the combination of two gametes both devoid of the factor for the blue colour.

The vitality of the gametes-combination and with it the average number of seeds per fruit and the germinating-power of the seed are more closely connected with the presence or absence in the gametes of the factor for the floral colour than with the nature of the plant, which produces the seed.

Groningen, 9 January 1914. *Botanical Laboratory.*

Anatomy. — "*The Arrangement of the motor roots and nuclei in the brain of Acipenser ruthenus and Lepidosteus osseus.*" By F. THEUNISSEN. (Communicated by Prof. L. BOLK).

(Communicated in the meeting of February 28, 1914).

In the Folia Neurobiologica of 1912 DROOGLEEVER FORTUYN [1]) described the arrangement of the motor roots and nuclei in the brain of an osseous Ganoïd: Amia calva.

He came to the conclusion that Amia in many respects resembled the Selachian type, though few points of analogy with the Teleosts were found.

Of the other Ganoïds as yet no adequate description exists as far as concerns the motor roots and nuclei. Valuable descriptions of the nervous system of Ganoïds are given by GORONOWITSCH [2]) and JOHNSTON [3]) (Acipenser), KINGSBURY [4]) and ARIËNS KAPPERS [5]) (Amia calva and Lepidosteus), but these articles contain rather a general account of the brain, the papers of JOHNSTON and KINGSBURY more specially of the sensory systems.

The Institute for Brainresearch possesses a complete series of the brain of Acipenser ruthenus, which has enabled me to study the relations of the motor system of this animal and to compare my results with those obtained by DROOGLEEVER FORTUYN in Amia Calva.

We are greatly indebted to Prof. MINOR in Moskow for our material of Acipenser ruthenus.

The results of my researches mapped out topographically after KAPPERS's method exhibit a striking resemblance with those obtained by DROOGLEEVER FORTUYN, and provide a new argument for classifying Amia with the Ganoïds.

My series, stained after WEIGERT-PAL with a contra-stain of paracarmine and alternating with a VAN GIESON series, enabled me to

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[1]) DROOGLEEVER FORTUYN, Notiz über den Eintritt der motorischen Nervenwurzeln in die Medulla Oblongata und über die Lage der motorischen Kerne bei Amia Calva, L. Folia Neurobiol. Bnd. VI, S. 27.

[2]) GORONOWITSCH Das Gehirn und die Cranialnerven von Acipenser ruthenus. Morphologisches Jahrbuch. Bnd. 13, 1888.

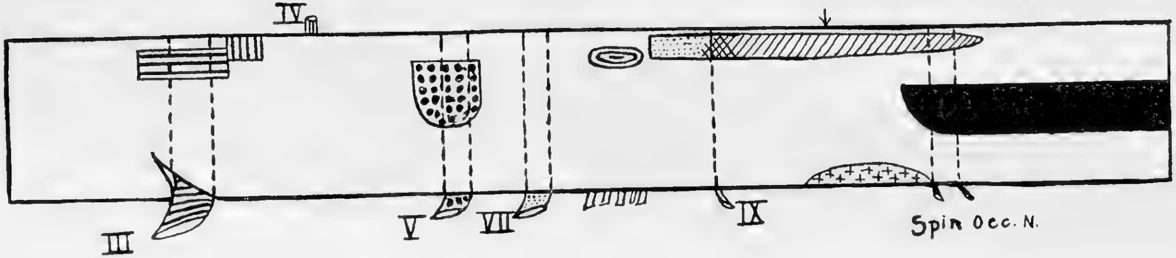
[3]) JOHNSTON, The Brain of Acipenser. G. FISCHER, Jena, 1901.

[4]) KINGSBURY, The structure and morphology of the Oblongata in Fishes. Journ. of Comp. Neur. Vol. VII.

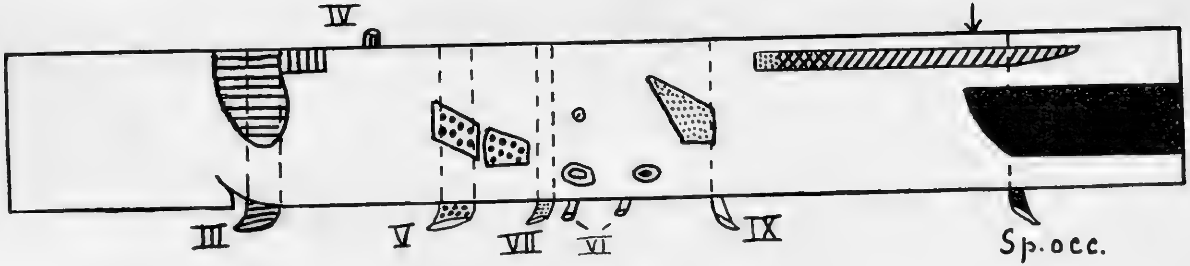
[5]) ARIËNS KAPPERS, Untersuchungen über das Gehirn der Ganoïden Amia Calva und Lepidosteus osseus. Abhandl. der Senck. Naturf. Gesellschaft in Frankfurt a. M. Bnd. 30, 1907.

EXPLANATION.

= nucl. paramedianus sive oliva inferior.



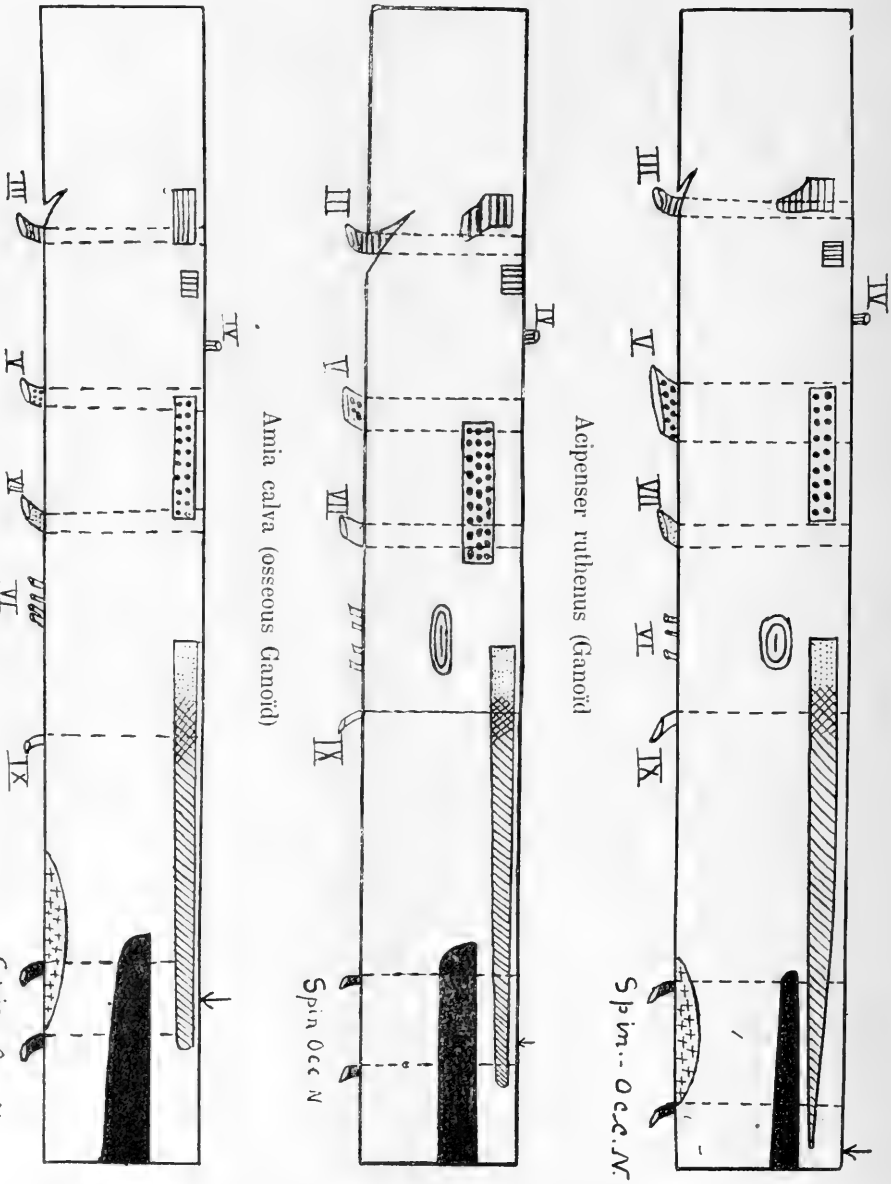
Scyllium (Selachian).



Tinca (Teleost).

Fig. 1. (The arrow indicates the place of the calamus scriptorius).

trace with a great amount of exactness the course of the motor roots and the position of their nuclei, which, brought in relation to the sensory systems of this animal, provided new contributions to the doctrine of neurobiotaxis.



Acipenser ruthenus (Ganoïd

Amia calva (osseous Ganoïd)

Lepidosteus osseus, 5 c.m. (osseous Ganoïd).

(Fig. 2). (The arrow indicates the place of the calamus scriptorius).

In Fig. 1 I give two reconstructions, one of a Selachian (Scyllium) and one of a Teleost (Tinca), and in Fig. 2 I give the topographical reproductions of the three Ganoïds as yet examined.

In Acipenser the III nerve enters the brain as usual directly behind the lobi inferiores. Its nucleus has a dorsal position, dorso-laterally from and between the fasciculi longitudinales dorsales; but very few cells reach a somewhat more ventral position than in scyllium, thus slightly indicating the process which in Teleosts gives rise to the formation of a real ventro-median nucleus. The same was the case in Amia. The dorso-lateral part of the nucleus extends some distance in front of the entrance of the III root.

Some distance in front of it, new cells of a much larger type appear, belonging to the large reticular type and probably constituting the homologue of Cajals[1]) "foco intersticial" in mammals and birds, also described by de Lange[2]) in Reptilia, which sends its axones in the posterior longitudinal fascicle.

The III nucleus finishes caudally near the posterior limit of its root entrance.

The IV nucleus lies some distance behind the III, separated from it by the tractus cerebello-mesencefalicus dorsalis, which passes here from the valvula cerebelli into the mesencephalon.

Such a separation has never yet been found in Selachii, but occurs rather often in Teleosts. The nucleus is small and its root lies a good deal farther caudad, as is also the case in Amia.

In the region of the trochlear nucleus large reticular cells are rarely found, and I get the impression that these large cells in Acipenser, as in other animals (v. Höevell)[3]), tend to group together in definite regions.

Also the position of the motor V nucleus shows a great resemblance with that of Amia, in so far as in both the nucleus retains a dorsal position over its entire length. The nucleus has moreover the same length in the two, though in Amia it begins a little caudad from the frontal line of entrance of its root and extends a little behind the VII root entrance.

Next to the trigeminus nucleus, along the lateral border of the fasciculus longitudinalis posterior, we find a great quantity of large

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[1]) El sistema nervoso del hombre y de los verte brados, Tomo II p. 551, Fig. 505 and Trabajos, Tomo VII: Ganglios de la substancia reticular del bulbo p 279 Fig. 9.

[2]) Das Zwischenhirn und das Mittelhirn der Reptilia. Folia Neurobiologica Vol. VIII p. 134, Fig. 57 and p. 135 Fig. 58.

Cyclostomes these large reticular cells have been found in front of the Oculomotor nucleus (comp. a. others Tretjakoff Arch. f. mikr. Anat. 1909, Bnd. 74).

[3]) J. J. L. D. Baron v. Höevell. Remarks on the reticular cells of the oblongata in different vertebrates. Proc. of the Kon. Akad. v. Wet. Amsterdam; April, 1911.

reticular cells. Whether these cells are connected with secondary neurones of the desc. V is difficult to tell. It seems as if several of their dendrites reach into the region of the sensory V.

It may be remembered that also van Höevell found a large quantity of reticular cells in the trigeminal and praetrigeminal region in the classes of vertebrates which he examined.

The VII root of Acipenser enters the bulb directly behind the motor V nucleus. After having reached the floor of the fourth ventricle it pursues its course in a median direction and successively shifts onto the lateral top of the fasciculus longitudinalis dorsalis, as is also the case in sharks, Teleosts and several Reptilia.

Where the motor VII root makes its caudal curve, that is in the region of the VIII, a group of large reticular cells is found next and under the fasciculus longitudinalis posterior, corresponding to van Höevell's nucleus reticularis medius.

The whole VII nucleus is continuous with the IX and X, with which it forms the posterior visceral column, as also occurs in Amia and in Selachii. A partial (Cyprinoïdae, Pleuronectidae) or total (Lophius) isolation of the VII nucleus from the posterior viscero-motor column as is found in Teleosts does not occur in Acipenser.

The posterior viscero-motor column has a dorsal position and extends a good distance caudad beyond the frontal limit of the spino-occipital column. It reaches farther caudad than in Amia, although neither here nor there a musc. trapezius is developed (Fürbringer)[1]). Consequently we may not consider the caudal part of this nucleus as nucleus accessorius as is the case in sharks.

More ventrally and more medially — near the ventrolateral border of the fasciculus longitudinalis posterior in and frontally from the region of the facialis nucleus the abducens-nucleus is found, which has three rootlets, which leave the brain between the VII and IX root. Just as in Amia the nucleus does not lie so ventrally as in Teleosts, nor is there a division into two chief groups as is fairly constant in bony fishes. The nucleus does not however lie as dorsally as in sharks.

The glossopharyngeus nucleus is continuous with the VII nucleus frontad and the X nucleus caudad. All its cells remain near the ventricle. The vagus nucleus has no special characteristics and resembles in every respect the nucleus of the IX. The spino-occipital column is the direct continuation of the motor column of the spinal

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[1]) Vergleichende Anatomie der Wirbeltiere mit Berücksichtigung der Wirbellosen.

cord. The two frontal rootlets are thin and their cells remain very dorsal, more as in Selachii than in Teleosts.

On the frontal level of the spino-occipital column a quantity of large reticular cells is found, which we may compare with the nucleus reticularis inferior in Rays. (Comp. VAN HÖEVELL). As in these animals a *central* inferior reticular nucleus (lying in the raphe, as occurs in all the higher vertebrates from Reptiles to Man) hardly occurs here: the cells keep a lateral position. Considering the differences which Amia as well as Acipenser exhibits when compared with Teleosts, we find as the most striking the less ventral position of the oculomotor and abducens nucleus and the absence of a division of the latter into two chief cell groups. A frontal isolation or ventral displacement of the VII nucleus does not occur.

All of these characteristics are easily understood if we compare the sensory systems and their reflex paths in these animals.

Concerning the less ventral extension or position of the III and VI nucleus, it may suffice to remark that the ventral tecto-bulbar tracts are not nearly so well developed in Acipenser (and Amia) as in bony fishes. The tectum opticum itself is relatively smaller (compared with the underlying midbrain and thalamus) than in most of the bony fishes and reminds us more of the condition found in sharks. No doubt this smaller development of the ventral tecto-bulbar paths is the reason of the less ventral migration of the eye muscle-nuclei mentioned above.

This fact may at the same time explain why the abducens nucleus keeps a relatively caudal position.

We know that a hypertrophy of the ventral tecto-bulbar tracts is not only correlated with a very ventral abducens nucleus, but equally causes a more frontal position, at least of its frontal division as is specially shown in Pleuronectidae [1]).

Concerning the position of the facial nucleus in these Ganoïds and its resemblance in this respect with Selachii the following explanation must be given:

In his excellent paper on Acipenser (l.c. p. 31) JOHNSTON remarks that from the sensory IX—X lobi (in which also the sensory VII root finishes) a secondary ascending fibres-tract runs along the descending V. According to his description, this tract (MAYSER's: "vagotrigeminale Bahn") is still unmyelinated in Acipenser, which

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[1]) Compare KAPPERS, The migrations of the V, VI, and VII nuclei and the concomitating changes in their root fibres. Verh der Kon. Akad. v. Wetensch. 1910, Deel 16, 2de Sectie, and Folia Neurobiol. Ergänz. Heft Vol. VI, 1912.

corresponds to our experience that this tract cannot be traced in Weigert-preparations.

In most Teleosts this tract is very considerably developed and HERRICK has described it there in a masterly way under the name of *ascending* secondary gustatory tract.

It is this tract which has the greatest [1]) influence on the ventral shifting and perhaps on the frontal isolation of the VII nucleus in Teleosts. It can even be demonstrated that the ventral migration of that nucleus (as well as of the V nucleus) is more conspicuous and more complete in those Teleosts, where this gustatory tract is more developed.

On account of this fact it is not astonishing that in animals where the *ascending* gustatory system is only relatively poorly developed a ventro-frontal migration of the VII nucleus has not yet occurred. It seems probable to me that in Ganoïds as in Selachii the secondary neurones of the sensory VII—IX—X nuclei are partly short intercalating neurones, while the longer secondary neurones of the viscerosensory nucleus may have chiefly a *descending* character.

It seems useful to me to give here also the topographic reconstruction of a young specimen of Lepidosteus osseus which the Institute received from Mr. EDW. PHELPS ALLIS in Menton.

I had at my disposition two specimens, of 5 and 10 c.m. The specimen of 5 c.m. being better preserved, I shall only give the reconstruction of this. I may add, however, that the 10 c.m. specimen did not differ in any principal point from this, so that I got the conviction that the definite arrangement of the motor nuclei is already present in the 5 c. m. specimen as far as concerns its principal features.

Also in Lepidosteus the oculomotor nucleus extends a considerable distance in front of the level of its root. The cells lie on the dorso-lateral border of the fasciculus longitudinalis, very near the ventricle. There is a difference in so far that the slight indication of a ventro-medial nucleus present in the fullgrown Amia and Acipenser fails in this young Lepidosteus. Perhaps this difference is due to the young stage of development.

As in the other ganoïds there is a considerable gap between the III and IV nucleus, although the tractus cerebello-mesencefalicus dorsalis does not run between it. [2]) The trochlear root lies again a good deal behind its nucleus.

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[1]) Not the only influence though. Some other tracts (e. g. an ascending sensory tract from the cervical region) may also run near the descending V.

[2]) Since there is no real valvula cerebelli in Lepidosteus this tract, if present, takes a more caudal course.

The trigeminus nucleus has the same dorsal position and length as in Acipenser and Amia. Its sagittal topography recalls rather that in Acipenser than in Amia.

The abducens leaves the same between the VII and IX roots with four rootlets as was the case in Amia.

The location of its nucleus could not be stated with exactness, the position of the cells being too diffuse amongst the reticular cells of that region. It resembles, however, the position in the other Ganoïds in so far as its cells do not form two well defined groups as occurs in bony fishes, nor do they have such a ventral position as in Teleosts. The posterior viscero-motor column has the same position as in the other ganoids. Its frontal limit is nearly the same, the caudal extension seems a little shorter, which may be due to the young stage of development.

It contains the motor VII, IX, and X nuclei, but the cells are not equally large everywhere: groups of large cells alternate with groups of smaller cells, of which the motor character is not so conspicuous. It may be that this means a little discontinuity in this motor column. It does not however give us sufficient evidence to speak of isolation of different nuclei.

The position of the spino-occipital rootlets and cells resembles very much that found in Amia.

On an average it may be said that Lepidosteus shows principally the same type in the arrangement of its motor roots and nuclei as the two other Ganoids.

A few words may be added concerning a structure at the base of the medulla oblongata near the spino-occipital rootlets: the *nucleus paramedianus* or *oliva inferior*.

In this region the dark aspect of the tegmental part of the bulb changes for a lighter one in the Weigert-Pal preparations, owing to an enlargement of the grey matter consisting of small, more or less spindle-shaped cells and a sort of "gelatinous" substance. The caudal and frontal limits of this structure are not sharp, but the bulk of it extends in the places indicated at the base of my topographic schemes by little crosses.

From this structure a crossed myelinated fibre tract runs along the lateral border of the oblongata to the region where the cerebellum joins the bulb. Also JOHNSTON (l. c. p. 16) describes such crossed fibrae arcuatae externae.

The character of this crossed cerebellar connection, the sort of cells that constitute the nucleus paramedianus and its topographic relation, prove that we have to consider it as a primitive oliva inferior.

It seems as if ventral axones coming from the spinal cord end in it. This caudal tract consists of thin fibres provided with only a small myeline sheath and makes the impression of being ascending in character.

Whether this can be a primitive homologue of HELLWIG's triangular tract, which occupies a similar position in the mammalian cord and oblongata, cannot be said.

It is interesting to see that this structure is already so well developed in the young Lepidosteus.

DROOGLEEVER FORTUYN has not indicated its limits in his map of Amia. It has neither been possible to me to mark its limits with any amount of exactness in this animal. The structure is so diffuse and little circumscript in Amia that its exact topography cannot be given in WEIGERT or VAN GIESON preparations. It is certainly smaller and less pronounced, which is not astonishing since Acipenser and Lepidosteus are excellent swimmers and Amia leads a more quiet life, as is also indicated by its name "mudfish". [1])

Resuming my results concerning the arrangement of the motor roots and nuclei in Acipenser and Lepidosteus, and comparing them with Amia on one side and with Scyllium and Tinca on the other, I may conclude:

Amia Calva, Acipenser and Lepidosteus osseus resemble each other closely, and differ as well from the Selachii as specially from the Teleosts.

They differ from the Teleosts by the very dorsal position of the motor VII nucleus and by the continuity of the motor column of the VII, IX, and X nuclei, by the less ventral position and more diffuse structure of the abducens nucleus, the entirely dorsal position of the V nucleus and the little ventro-medial migration of the oculomotor nucleus. On an average they resemble much

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[1]) I will call attention to the possibility that the nucleus paramedianus of fishes is rather the homologue of the ventro-medial accessory olive than of the regular oliva inferior (comp. also KAPPERS, Folia Neurobiologica Sommerergänzungsheft, Bnd. VI, 1912) on account of the fact, mentioned by BROUWER (Archiv. Psych. Bnd. 51), that the ventro-medial accessory olive has connections with the vermis cerebelli, not with its hemispheres, and that the cerebellum of sharks and other fishes is probably the homologue of the vermis.

It is an interesting fact that this ventro-medial accessory olive of mammals enlarges greatly in cetaceans, where it is again the dominating part of the inferior olive (comp. KANKELEIT, Zur Vergl. Morphologie der unteren Säugetier-olive, Inaug. Diss. Berlin 1913). This, and the fact that in fishes it is probably the only part of the inferior olive that occurs, might lead us to believe that the ventro-medial accessory olive is chiefly related with the musculature of the trunk and the tail.

more the selachian type of arrangement from which they only differ by the constant gap between the oculomotor and trochlear nucleus, the more dorsal position of the trigeminus nucleus and the less dorsal extension of the abducens cells and roots.

Physiology. *"On esophageal auscultation and the recording of esophageal heart sounds".* By Dr. C. E. BENJAMINS. (Communicated by Prof. Dr. H. ZWAARDEMAKER).

(Communicated in the meeting of February 28, 1914).

When performing an esophagoscopy our notice is surprisingly attracted by distinct considerable pulsations at 32—35 c.m. from the incisor teeth. Here an expansion may repeatedly be seen to appear and to disappear rapidly after some complex to-and-fro motions. Anatomically it has been shown that in this very place the left auricle is located against the esophagus, from which it is separated only by the pericardium, and, therefore, admits of immediate experimentation.

Following the lead of RAUTENBERG [1]) and MINKOWSKI [2]) I availed myself of this circumstance by taking along this path cardiograms as illustrated in Fig. 5. The results achieved in this investigation, which was conducted in a way differing from the method generally employed, will be given elsewhere. In this paper I propose to publish my experience about the esophageal heart sounds.

I first wish to give some preliminary details of the technique of examination. To the extremity of a strong grey india-rubber tube (75 c.m. long; 5 m.m. bore; thickness of the rubber 1 m.m.), graduated from 20—40 c.m., a knob-shaped appendage is fitted. Over this appendage a rubber finger stall (from which the hard rim has been removed) is tied so as to leave an elongation of 3—4 c.m.

The subject, whose pharynx had, or had not, been sprinkled beforehand with a spray of a 5 $^0/_0$ cocain solution, to which some drops of adrenalin had been added, swallows the lubricated tube without difficulty, only being aided a little as at the insertion of a stomach tube. When the tube is inserted as low as ± 35 c.m. from the labial curve, it is adjusted by means of a ⊤-piece to the binaural stethoscope. (The ⊤-piece has to protect the tympanic membranes the moment the subject displays signs of choking). When he keeps quiet, the ⊤-piece is closed with the finger, so that we hear distinctly

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[1]) RAUTENBERG. Die Registrierung der Vorhofpulsation von der Speiseröhre aus. Deutsches Arch. f. klin. Medicin 1907. Bd. 91. S. 251.

[2]) O. MINKOWSKI. Die Registrierung der Herzbewegungen am linken Vorhof. Berl. klin. Wochenschr. 1907. No. 21.

all the sounds in the chest. In order to examine the heart sounds the subject must hold his breath for a few seconds.

It requires some practice to distinguish the heart sounds. At first a confusion of rustling, blowing, and crackling sounds is heard. However, the moment the subject holds his breath only the well-marked heart sounds can be made out, and then we become conscious of *four murmurs, not two.* When first listening to the two loudest more defined sounds we distinctly hear one long, coarse sound, and a second which is short and faint: the ordinary type of the heart sounds over the apex. If we can divert our attention from these sounds and try to single out the two much softer murmurs, which seem to come from afar, we become aware that the first of them *commences before the first ventricular sound and undoubtedly runs up till the latter is heard and even seems to coincide with it for a short time. In the pause between the first and the second ventricular sound an additional short and faint murmur is noticeable.*

Passing the tube lower down or moving it a little higher up causes the two faint murmurs to disappear, in order to re-appear again, whenever contact with the auricle is again effected.

No doubt, we are here dealing with the auricular sounds that have given rise to so much controversy. To raise the plausibility of this assertion, I may add that, with persons subjected to esophagoscopy, the site of the auricle was ascertained by measurement and that it was always at this very spot that the auricular sounds occurred. Besides the four murmurs under consideration one of our subjects exhibited a fifth faint murmur, taking place after the second ventricular sound. It may be typified as follows: 

It appeared to me essential that these auricular sounds should be recorded.

The chief obstacle was that, besides the sound vibrations impulses arise from the movement of the heart, viz. at the apex beat, owing to the impact against the chest-wall, and along the esophageal path in consequence of the pressure on the rubber ball. Various methods have been suggested to preclude the passage of these foreign impulses. **Einthoven** [1]) and his pupils made the tube, connecting the

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[1]) W. **Einthoven** and **Geluk**. On the recording of heart sounds. Researches in the physiol. lab. of Leyden. Sec. Series 1896.

G. **Fahr**. On simultaneous records of the heart sounds and the electro-cardiogram. Heart. Vol. 4. No. 2. 1912.

P. J. T. A. **Battaerd**. Further graphical experiments on the acoustic phenomena of the heart.

Dr. C. E. BENJAMINS: „On esophageal auscultation and the recording of esophageal heart sounds."

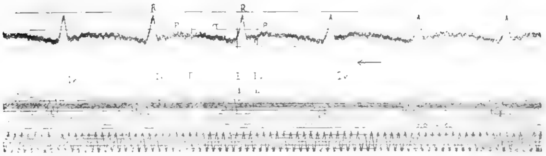

Fig. 2

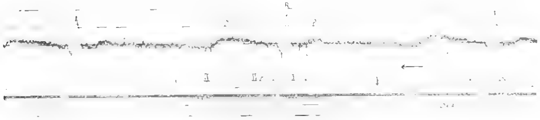

Fig. 3

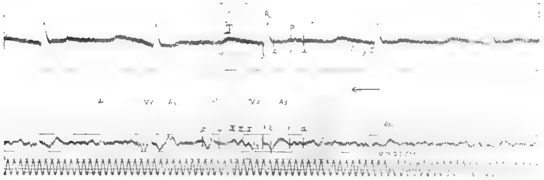

Fig. 4

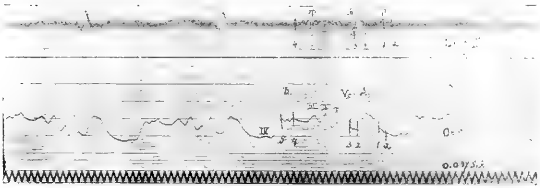

Fig. 5

stethoscope with the recording apparatus, to communicate with the air of the room through a side opening, so that the impulses were allowed to escape. Gerhartz1) points out that, though this contrivance may enfeeble the sound as well as the extraneous impulses, it does not eliminate the latter altogether. In the different heart-sound figures he clearly sees indications of the apex-beat.

Still, considering the extremely beautiful curves taken in Einthoven's laboratory, I daresay his method will do for recording heart sounds through the chestwall; not, however, for registering them along the esophagus. It soon became evident that the jerky compressions of the rubber-ball could not be excluded from the curve. For esophageal records the insertion of a stout stiff membrane serves our purpose better. Various glass and mica membranes were tried, but discarded as either enfeebling the sound or permitting the accidental impulses to be recorded along with the heart sounds. Then a common phonendoscope on a solid ebonite plate was inserted; I chose this material because it had proved to transmit heart sounds. The phonendoscope *P*, in leaden case (*o*), was attached hermetically to an afferent tube and had thus been adapted for a circuit with esophagus tube and microphone. If the second aperture was left open, no effect was produced on the recording apparatus either by blowing into the tubes or by squeezing them. It is certain, therefore, that the ebonite membrane is not thrown into vibration by the impulsive beats of the air. Our greatest obstacle was now overcome. It is true, the sounds were considerably weaker, but what we wanted to hear, was clearly audible. For further records we used a microphone (in camera plumbica) and a small string galvanometer. This combination had in previous researches proved suitable for recording the low sounds. (For the heart sounds Weisz2) and Gerhartz determined the number of vibrations at 50—100).

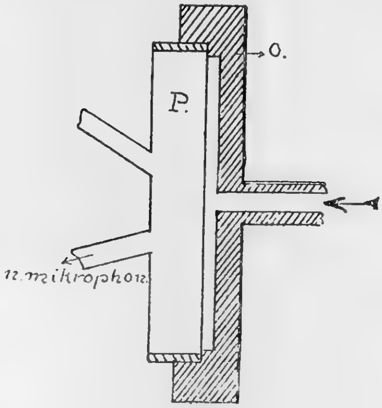

Fig. 1.

At the same time the electrocardiogram was taken in lead II by means of the large string galvanometer, with an arc-light of its own. With the aid of a screen the cone of either lamp was intercepted,

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1) K. Gerhartz. Die Registrierung der Herzschalles. Berlin 1911.

2) O. Weisz. Phono-kardiogramme. Gaupp und Nagel's Sammlung No. 7 Jena 1909.

so that each lamp directed its light upon one half of the field. Likewise the esophagogram was sometimes taken simultaneously.

Fig. 2 (a cardiogram taken from Miss B.) is illustrative of the slight oscillations of the heart sounds. Because we directed all our attention to the heart sounds, no notice was taken of the electrocardiogram, which accounts for its unsatisfactory record. However, for the present it serves our purpose. At *Iv* we observe most distinctly a constant, rather slow vibration of the string, *which occurs before the systolic portion of the electrocardiogram and is, therefore, of auricular origin.* (In the experiments, advisedly arranged, the recording apparatus exhibited only a scarcely measurable slowing). Here then we managed to record part of what is perceived by the ear. It does not amount to much; the second auricular sound is wanting, but the recording apparatus, on which moreover only weakened sounds are directed, will ever be inferior to our highly sensitive ear. It follows, that from these curves we cannot identify the real commencement and the real termination of the heart sounds, the initial and the terminal vibrations not having been well represented in the tracing.

Of the first auricular sound only the loudest portion has been traced. The ventricular sounds, which are much louder, yield much better tracings and confirm EINTHOVEN's experience with regard to the form of the heart sounds. They also point to his method being perfectly reliable for the sounds through the chestwall, since we gather from them that the first auricular sound is made up of three phases (a slow initial vibration, then the rapid main vibrations and finally a slower terminal oscillation), whereas the second sound consists of rapid vibrations only. We found the period of vibration of the first auricular sound to be rather low, viz. 50 per second. Further particulars are shown in Fig. 3, taken from subject t. D.; however, here also the amplitudes are small, owing to considerable damping. First of all we observe in one heart-rhythm three well-defined groups of large vibrations. I and II represent the ordinary ventricular sounds and commence at the familiar spots, viz. somewhere about *S* and at the end of *T*. The vibrations preceding I start at a point some way from the foot *Q* of the *R*-peak, and must, of course, be of ventricular origin. I marked them *Iv*. A couple of slight vibrations at *X* indicate the real commencement. It will be seen that the first sound like the first ventricular sounds is made up of different parts, with differing vibration frequency. At the end of the first ventricular sound we observe a couple of unlooked-for slow vibrations (II*v*) with the shortest possible gap between them.

Here I have been fortunate enough to record the short and faint second auricular sound.

At the auscultation this subject often exhibited clearly GIBSON-EINTHOVEN's third sound. In accordance with this I notice at ↓ a faint vibration of the string, which for the rest is perfectly quiet. However the tracing is not clear enough to convince others.

I have also endeavoured to record the heart murmurs by taking a superimposed curve, as suggested by GERHARTZ. If, for instance, we leave the impulses to themselves, the recording apparatus will take a cardiogram in which the more rapid vibrations of the heart sounds are represented.

The esophagus tube being directly in circuit with the microphone, with a side opening though, yielded the cardiogram (Fig. 4), taken from subject *P.* In it we discern all the features of the so-called complex esophagogram as instanced in Fig. 5 for comparison.

The apex of the auricle is indicated by *As*; *Vs* is the ventricular apex; *D* the diastolic portion of the third elevation.

The systolic apices I, II, and III, which are so prominent in both curves, I shall not discuss any further in this communication. The points 1 to 5 are to be found in both tracings. A wave IV in the diastole, visible only in Fig. 5, I shall revert to later.

Though, for the rest, the string is rather quiet, we observe, especially with the aid of a magnifying glass, at the site of the first and the second auricular sound, vibrations which have been superimposed in the curve. Moreover at the auricle apex a good many fine oscillations are discernable together with some bolder amplitudes. *These are the vibrations of the first auricular sound, which run up to the commencement of the ventricular contraction.* Though less prominent, some vibrations, originating from the second auricular sound, are noticeable in the descending limb of peak I.

Now, how are these auricular sounds produced?

It has been generally admitted now, that heart sounds result from muscle murmurs, from vibrations of membranes (valves or cell-walls) and from eddies. An explanation for the first auricular sound is soon found. Most likely it is chiefly due to muscular contraction, but *then the auricular contraction must last till the ventricular systole,* more particularly till the closure of the atrio-ventricular valves. The continuance of the auricular systole in the isoelectric portion of the electrocardiogram, between *P* and *Q*, is moreover demonstrated by the fact that the largest vibrations of the auricular sound fall in this portion, nay the systole is even prolonged for some time while the *R*-peak is being formed (Fig. 3).

When scanning the esophagogram I was led to think that the auricular systole runs into the ventricular systole without a previous dilatation. This view is borne out by the auscultatory results and the record of the auricular sounds.

Indeed, formerly it was taken for granted that only with cold-blooded animals, e. g. the frog, the ventricular systole commences only when the auricular systole has been completed, but that with mammals the relations are more complex.

In **Donders'** Physiology 2nd Edition 1859 page 27 I read: "dasz bei jedem Rhythmus zunächst die beiden stark ausgedehnten Vorhöfe sich zusammenziehen und gleich darauf die beiden Kammern, ferner *die Vorhöfe sowohl wie die Kammern einen Augenblick im contrahirten Zustande verharren*". **Donders** holds that the old theory of **Haller**, viz. that the auricular contraction and the ventricular systole occur alternately, has been disproved. **Schiff**'s experience coincides with this view. It is remarkable that, in spite of this, **Haller**'s theory has found favour again in physiology. The second auricular sound cannot be accounted for so easily; it may be that eddies come into play; it has also been suggested by D. **Gerhardt** (cited by **Wenckebach** l. c.) that it may possibly proceed from muscular movement at the auricular diastole.

The foregoing evidence has set the conjectures at rest concerning the first auricular sound, which has long been a subject of dispute in the literature. By what has been brought forward here **Krehl**'s [1]) experience has been confirmed, **Hürthle**'s [2]) "Vorton", recorded by many researchers, has been substantiated; **Fahr**'s [3]) initial vibrations have been transferred to the auricular systole; the discoveries of auricular sounds by **Battaerd** [4]), **Weisz** [5]) and others have been sustained, while moreover a second auricular sound has been added.

Finally I wish to return once more to the diastolic sound mentioned heretofore. I presume this to be the third sound of **Gibson-Einthoven**. **Gibson** [6]) detected in some individuals, with slow hearts, an additional wave, called "b" in the diastolic portion of the curve of the jugular vein and occasionally he heard a very feeble third

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[1]) L. **Krehl**. Ueber den Herzmuskelton. Arch. f. (Anat. u.) Physiol. 1889.

[2]) K. **Hürthle**. Ueber die mechanische Registrierung der Herztöne. Pflüger's Arch. Bd. 60 S. 263.

[3]) G. **Fahr**. l c.

[4]) P. J. T. A. **Battaerd**. l.c.

[5]) O. **Weiss**. l.c.

[6]) A. **Gibson**. The significance of a hitherto undescribed wave in the jugular pulse. The Lancet, Nov. 16, 1907.

sound. EINTHOVEN [1]) found that third sound in his records as a faint vibration, at a distance of 0,13 sec. from the commencement of the second sound. In our subject, who has a slow heart (from 60 to 70 per minute) I, very often, *but not always,* noted this third sound as a faint diastolic murmur, which *got more distinct when the tube was slipped as far down as* 38 *c.m.* In fact the venous pulse of this person often, though not always, yielded a beautiful GIBSON "*b*"-peak in the diastolic portion of the cardiac cycle.

It is evident, therefore, that it is of ventricular origin. If we return again to Fig. 5, the esophagogram of the same subject, and look at wave IV in the diastole at 0,135 sec. after line 4, the place of the closure of the semilunar valves, we shall observe that this place corresponds to the site of EINTHOVEN's third sound.

FRÉDÉRICQ [2]) also sometimes found a similar diastolic wave in the auricular-pressure tracings.

When putting these facts together, viz. 1 ventricular origin; 2 inconstancy; 3 wave in the auricular-pressure tracings; 4 wave in the esophagogram; 5 wave in the venous pulse curve; GIBSON's explanation seems to me the most plausible. He ascribes the origin of this third sound to the fact that, at a high pressure or at a copious onflow of blood into the veins, the atrio-ventricular valves will close for some moments just before the diastole, on account of the blood rushing into the ventricle during the diastole, in consequence of which the membranes are swung up by the eddies. They produce a short sound and slightly check the blood in its passage to the ventricles.

The evidence presented in this article will, I hope, support the view that, together with the esophageal cardiography, the auscultation and the recording of heart sounds through the esophagus yields results not obtainable through the chestwall.

Physics. — "*A new relation between the critical quantities, and on the unity of all the substances in their thermic behaviour.*" (Continued.) By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of March 28, 1914).

13. If in the found [3]) expression $b = f(v)$, viz.

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[1]) W. EINTHOVEN. A third heart sound. Ned. Tijdschrift voor Geneesk. 1907 Vol. 2 p. 470.

[2]) L. FRÉDÉRICQ. La seconde ondulation positive (première ondulation systolique) du pouls veineux physiologique chez le chien. Arch. intern. de Physiol. 1907.

[3]) These Proc. XVI, p. 924 to be cited as II.

$$\left(\frac{b-b_0}{b_k-b_0}\right)^n = \frac{x_k - b'_k\left(\frac{x}{x_k}\right)^n}{x_k - b'_k}, \quad . \; . \; . \; . \; . \; . \quad (30)$$

in which $x=(b-b_0):(v-v_0)$ — and which except v_0 and $b_0\,(=v_0)$ only contains critical quantities which are (directly or indirectly) experimentally determinable — we introduce again b_g-b_0 instead of b_k-b_0, then when ($30b$) is taken into account, viz.

$$\left(\frac{b_k-b_0}{b_g-b_0}\right)^n = 1 - \frac{b'_k}{x_k}\quad , \; . \; . \; . \; . \; . \; . \quad (30b)$$

(30) passes into

$$\left(\frac{b-b_0}{b_g-b_0}\right)^n = 1 - \frac{b'_k}{x_k}\left(\frac{x}{x_k}\right)^n .$$

In this is, also according to ($30b$):

$$x_0{}^n = Lim\left(\frac{b-b_0}{v-v_0}\right)_0 = x_k^{n+1} : b'_k\,,$$

so that after substitution the equation (29), i.e.

$$\left(\frac{b-b_0}{b_g-b_0}\right)^n = 1 - \left(\frac{x}{x_0}\right)^n, \quad . \; . \; . \; . \; . \; . \quad (29)$$

is found back, from which we had started. In this we have found for the exponent n [see ($30a$) and (31)]:

$$n = \frac{1-x_k}{x_k-b'_k} = \frac{8\gamma\,(\gamma+1)}{(2\gamma-1)\,(4\gamma+1)} = \frac{2b_k\,v_k}{(b_k-b_0)\,(2b_k+b_0)},$$

when for b'_k its value $(b_k-b_0)^2 : b_k\,v_k$ is substituted, and further for $b_k:b_0$ the value 2γ found in I[1]) (see § 6, p. 817) and for $v_k:v_0$ the value $2\,(\gamma+1)$. In this v_0 is the liquid volume extrapolated from the equation of the straight diameter at $T=0$, γ being the reduced coëfficient of direction of the straight diameter.

In the two foregoing Papers the problem with which I have been continually occupied since 1901, has been brought to a provisional solution. Already then I expressed (Arch. Teyler (2) VII, 3^{e} partie: "Sur l'influence des corrections etc.") the critical quantities in the values of b'_k and b''_k at the critical point (see among others loc. cit. § 4), and verified the function $b=f(v)$ proposed by KAMERLINGH ONNES for H_2 and CO_2. We now know that this function does not fulfil the condition that at T_k the quantities b'_k and b''_k must have the values found by me. (See the preceding Paper II.)

In 1905 I went further, and expressed the different critical quantities in two auxiliary quantities α and μ, of which α was in relation with f, and μ represented $1:s$. (See particularly § 2 of

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1) These Proc. XVI, p 808 to be cited as I.

the article in the Arch. Teyler (2) IX, 3^e partie: "Quelques Remarques sur l'équation d'état").

This is therefore exactly the same as VAN DER WAALS continued years later[1]), quite independently of the above investigations, and in which he found several remarkable approximate relations. These were afterwards brought to a more accurate form by me, through the introduction of the quantities λ_1 and λ_2 into the expressions for RT_k and p_k, in which it appeared that $\lambda_1 = \lambda_2$ for ordinary substances amounts to about 0,98, and approaches to 1 as the substances approach more and more to so-called "ideal" substances with b little variable or invariable. (See also I).

Thus all the quantities were expressed in f and s. But in consequence of the equalization of λ_1 and λ_2 all of them could also be expressed in the one quantity f (or rather $f' = f : (1 + \varphi)$ — see I p. 811 and p. 814). This further step was followed by a still more decisive one in consequence of a new relation being found (See I, p. 815 et seq.), on account of which everything could be expressed in the one quantity γ[2]); the reduced coefficient of direction of the straight diameter[3]). For $b_k : v_0$ appeared to be $= 2\gamma$ (p. 816 loc. cit.). Of special importance is the simple relation $\underline{f' = 8\gamma}$ (p. 818).

The table on p. 819 was the result of these new considerations.

And now that we have also an idea of the course of the function $b = f(v)$ — though of course the found relation (30) or (29) is not the *only* one that satisfies all the imposed conditions, but certainly one of the simplest relations that can be put — now the temperature-influence neglected up to now, forces itself upon our attention. For the found expression (29) only holds for one temperature, viz. for the *critical*. Here too we shall have to be satisfied for the present with an empirical relation, leaving it to future investigation to give the found equations $b = f(v)$ and $b = f(T)$ a theoretical foundation, in which then the relations, found in I between b_k and v_o (b_0), and those for b'_k and b''_k, will find a natural explanation.

14. *The variability with respect to T.*

In the expression (30) the quantities $b_k : b_0$ and $v_k : v_0$ occur besides in the first member also in the second member because of x_k and b'_k and the exponent n. In this $b_k : b_0 = 2\gamma$ and $v_k : v_0 = 2(\gamma + 1)$.

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[1]) These Proc. XIII, p. 118, 1216 et seq.

[2]) These Proc. XIV, p. 771 et seq.

[3]) And through which some approximate relations of V. D. W. (These Proc. XV, p. 903, 971 and 1131) which were based on the approximate equality of s and s' (which quantities can, however, differ more than 12%) could be replaced by more accurate ones.

The value of $b_k : b_0$ (and of $v_k : v_0$), i. e. of γ, will depend on the value of the *critical temperature* for *different* substances. But for *one and the same* substance, considered at different temperatures, $b_k : b_0$ (and $v_k : v_0$) loses of course its significance outside T_k. This is, however, not the case with $b_g : b_0$, which quantity is in relation with $b_k : b_0$ through (30^b) at the critical temperature. We have namely :

$$(b_g-b_0)_k=(b_k-b_0)\sqrt[n_k]{\frac{x_k}{x_k-b'_k}}.$$

If in this we substitute the value $2\gamma_k-1$ for $(b_k-b_0) : b_0$, the value $(2\gamma_k-1) : (2\gamma_k+1)$ for $x_k=(b_k-b_0) : (v_k-v_0)$ and the value $(2\gamma_k-1)^2 : 4\gamma_k(\gamma_k+1)$ for b'_k — see above, and also I, p. 818 — we find after some reductions :

$$\left(\frac{b_g-b_0}{b_0}\right)_k=(2\gamma_k-1)\sqrt[n_k]{\frac{4\gamma_k(\gamma_k+1)}{4\gamma_k+1}}, \quad . \quad . \quad . \quad (33)$$

in which $n_k=8\gamma_k(\gamma_k+1) : (2\gamma_k-1)(4\gamma_k+1)$, according to (31) of II.

This naturally suggests the idea of making the above considerations more general by putting $b_g : b_0=2\gamma'$; so that not only at the critical temperature the equation (33) holds, in which γ_k represents the reduced coefficient of direction of the straight diameter in the neighbourhood of T_k — but quite general at any arbitrary temperature the relation

$$\frac{b_g-b_0}{b_0}=2\gamma'-1=(2\gamma-1)\sqrt[n]{\frac{4\gamma(\gamma+1)}{4\gamma+1}}, \quad . \quad . \quad . \quad (34)$$

in which, therefore, for an arbitrary substance γ varies together with γ', when T changes.

Then outside T_k the quantity γ is no longer in relation with any $b_k : b_0$ or with the reduced coefficient of direction of the straight diameter in that point — but yet represents for any arbitrary temperature: the value of $^1/_2\,(b_k : b_0)$, or of the said coefficient of direction, for *another substance for which the critical temperature would correspond with that temperature.* Thus also outside T_k something is left of the original meaning of γ.

So passing from $T=0$ to $T=\infty$ for *one and the same* substance all the types will be met with, which are found for *different* substances at their critical temperatures. *Every* substance approaches the *ideal* type with constant b, when only the temperature is made to approach to 0 ; *every* substance approaches the limiting type of the substances with high molecular weight ($\gamma_k=1$), if only the temperature be taken high enough. This has already been fully explained in I (see § 7, p. 820—821), and there is no call to repeat the explanation here.

Remark.

Before proceeding to the discussion of the dependence on the temperature of γ' and γ, a remark may be made in this context, concerning the necessary consequences of the above considerations with regard to the course of the *"straight diameter"*. When namely for a substance we descend from the critical temperature to lower temperatures, $b_g - b_0$, so also γ, will continually descend; so that the slope of the straight diameter for an arbitrary temperature (which slope at every temperature will depend on the type of the isotherm at the considered temperature, determined there by $b_g - b_0$), will also have to *decrease* from the value γ_k measured at T_k down to the lowest value, i. e, $\gamma = {}^1/_2$, holding for an ideal substance ($T_k = 0$). In other words the straight diameter cannot possibly remain *straight*, but will exhibit such a curvature, that the final direction at $T = 0$ (supposing that liquid volumes could still be realized at these low temperatures) approach to about 0,5.

It is self-evident that the *law* according to which this decrease takes place *need* not be the same as the law that determines the decrease of γ' or γ with the temperature, since for one and the same substance γ_k at the *critical* temperature is, indeed, in direct relation with the course of the straight diameter there, but this is no longer the case, of course, below the critical temperature, where $b_k : b_0$ and γ have lost their original meaning. A *separate* investigation will have to decide later on, what the relation is of the real direction of the straight diameter below T_k, and the temperature.

That the change of direction for *ordinary* substances will never be very great, however, at least not in the beginning, follows from this that according to the law of variability of γ to be drawn up presently — with which the variation of direction of the straight diameter in any case will run *parallel* — a decrease of γ of any importance will not take place until at *lower* temperature, i. e. at temperatures which are considerably lower than the critical. For substances as Hydrogen and Helium, where the critical temperature lies so near the absolute zero, a *more pronounced* curvature of the straight diameter will of course be expected.

15. *A relation between γ_k and T_k.*

It was then found by me that the quantity γ_k at T_k, i. e. the (reduced) coefficient of direction of the straight diameter, is in a very simple relation to T_k, namely according to the relation

$$\underline{\frac{b_k - b_0}{b_0} = 2\gamma_k - 1 = 0{,}038 \sqrt{T_k}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

It may appear from the following table with what accuracy the value of the quantity γ_k is given by this simple formula.

	T_k	$\sqrt{T_k}$	$2\gamma_k-1$	γ_k calculated	γ_k found
Helium	5.2	2.28	0.0866	0.543	± 0.56
Hydrogen	32.3	5.68	0.2158	0.608	0.604
Argon	150.65	12.27	0.4763	0.738	0.745
Xenon	289.7	17.02	0.6468	0.823	0.813
Acetylene	308.5	17.56	0.6673	0.834	0.858
Isopentane	460.9	21.47	0.8159	0.908	0.914
Fluorbenzene	559.6	23.66	0.8991	0.950	0.933

This table requires some elucidation. Of the many substances whose values were at my disposal, I have only chosen some *typical* ones, namely those substances which, just as in the table in I, p. 819, represent a *class* as far as the value of γ_k is concerned. Oxygen has not been inserted, because we know already from I, p. 819 that according to the values of s and f found for O_2 the value of γ_k would have to be about 0,72, whereas 0,813 was found, just as for Xenon. We have ascribed this to association. Also for CO_2, which belongs to the class of acetylene, the formula yields too low a value of γ_k, viz. 0,85, whereas 0,9 was found. Whether here too association of the liquid is the cause, is unknown to me. To the iso-pentane group belongs also n-pentane and other substances, of which T_k lies in the neighbourhood of 460° or 470° (absolute), and γ in the neighbourhood of 0,90 or 0,92. For iso-pentane $\gamma_k = 0{,}916$ according to YOUNG. The value given by us in the table, viz. 0,914, is a mean value. Also C_6H_6, CCl_4, and such substances with T_k in the neighbourhood of 550° or 560° absolute, and $\gamma_k = 0{,}93$ or 0,94 belongs to the Fluorbenzene group. The given value 0,933 is again a mean value.

For H_2O, of which $T_k = 638$, $\sqrt{T_k} = 25{,}26$, a value 0,98 would follow for γ_k $(2\gamma_k - 1 = 0{,}96)$. It is unknown to me whether experimentally a sufficiently established value of γ_k for water is known; probably it will again be greater than 0,98, because also H_2O is associated, although it be at lower temperatures than the critical.

Even for a substance with a critical temperature of 900° γ_k would be only 1,07 according to (35). However — at very high temperatures $b_k : b_0$ and so also $b_g : b_0$ will approach to a *limiting value*, so that the coefficient 0,038 for $\sqrt{T_k}$ will probably gradually decrease at higher temperatures. But as yet nothing is known about this, and I shall therefore refrain from giving a more general expression derived from theoretical considerations founded on the calculus of probabilities (statistical mechanics), of which (35) or rather (36) would only be a special case, holding only for temperatures up to about 600° absolute. This expression too is characterized by particular simplicity.

Finally some indications of the sources of the given values of T_k and γ_k (found).

Helium. The value of $T_k = 5{,}2$ is that of KAMERLINGH ONNES in Comm. 124 (see also Suppl. N° 21). The earlier values given in Comm. 102*a*, 112, and 119 deviate but little from this final value. The value of γ_k (found) follows from that given for f in Comm. 124, viz. 4,46 as lowest limit. If f is identified with f', which is certainly permissible here on account of the slight variability of b for Helium, $\gamma_k = {}^1/_8\, f = 0{,}56$ would follow from $f' = 4{,}5$. I do not know a direct determination of γ_k.

Hydrogen. In Comm. 119 is given $T_k = 32{,}3$. From $f = 4{,}83$ (see KUENEN, die Zustandsgleichung, p. 142) would follow $\gamma_k = 0{,}604$. I do not know a direct determination of γ_k either.

Argon. According to Comm. 115, $T_k = -122{,}44 + 273{,}09 = 150{,}65$. By direct observation (Comm. 131) $\gamma_k = 0{,}7446 = 0{,}745$[1]) was found here.

Xenon. Here I find given $T_k = 16{,}6 + 273{,}1 = 289{,}7$, and further $\gamma_k = 0{,}813$, as the boundary line coincides entirely with that of O_2, where $\gamma_k = 0{,}813$.

We may therefore with close approximation draw up the formula $2\gamma_k - 1 = 0{,}038\,\sqrt{T_k}$ for substances, the critical temperature of which lies no higher than ± 600° absolute (330° C.), and with extension to arbitrary temperatures:

$$\underline{2\gamma - 1 = 0{,}038\,\sqrt{T}} \quad \ldots\ldots\ldots \quad (35a)$$

For $(b_g - b_0) : b_0 = 2\gamma' - 1$, also holding when a substance is considered at arbitrary temperatures, and not only at the critical, we may put:

$$\underline{\frac{b_g - b_0}{b_0} = 2\gamma' - 1 = 0{,}041\,\sqrt{T}} \quad \ldots\ldots\ldots \quad (36)$$

---

[1]) From $s = 8\,\gamma_k : (1 + \gamma_k) = 3{,}424$ (Comm. 131) would follow $\gamma_k = 0{,}748$, which is in perfect harmony with the found value.

For every value of γ we may calculate the corresponding value of $(2\gamma'-1):(2\gamma-1)$ from (34), bearing in mind that $n=8\gamma(\gamma+1):(2\gamma-1)(4\gamma+1)$. We shall then find the mean value 1,08 for that ratio, so that the factor of $\sqrt{T}$ will get an average value of 0,038 (which also represents a mean value) $\times$ 1,08 = 0,041.

In this it will no doubt follow from the nature of the thing that the factor 0,041 in the formula for $b_g - b_0$ is the same for all the substances, but the factor 0,038 in the formula for $b_k - b_0$ varies somewhat with different substances, dependent on the value of the ratio $(b_g - b_0):(b_k - b_0)$. For b_g is, so to say, a *natural* point in the series of values between the final points b_0 and b_g — but b_k only an accidental point, dependent on the situation of the critical point. It follows, however, from this that now, for Helium e.g., the factor for $(b_k - b_0):b_0$ will become greater than 0,038, viz. $0,041 : 1,004 = 0,041$, because for He the value of $(b_g - b_0):(b_k - b_0) = 1,004$. But this does not present any difficulty, for He can very well have a somewhat greater value of the factor. With 0,041 $2\gamma_k - 1$ would namely become $= 0,0931$; so $\gamma_k = 0,547$, only little higher therefore than 0,543, and still smaller than 0,56.

For the sake of completeness I shall just give the corrected values of γ_k (calculated) for the other substances mentioned in the table. For H_2 γ_k would become $= 0,615$. (Here the reduction factor $\theta = (b_g - b_0):(b_k - b_0) = 1,011$). For Argon we find $\gamma_k = 0,739$ (with $\theta = 1,053$); for Xenon with $\theta = 1,077$ we find the value 0,824 — both almost identical with the values in the original table. C_2H_2 yields $\gamma_k = 0,832$ with $\theta = 1,084$; Isopentane $\gamma_k = 0,897$ with $\theta = 1,11$; Fluorbenzene finally gives $\gamma_k = 0,933$ with $\theta = 1,12$. The last value of γ_k is now also equal to the "found" value of γ_k.

16. *Calculation of the theoretical b-values.*

The values of b can now be calculated from the reduced equation of state in the form [see I, p. 812, equation (*c*)]:

$$\left(\varepsilon + \frac{f'-1}{n^2}\right)(n - \beta) = s\,m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (37)$$

In this β represents $b : v_k$. The values found thus can then be compared with those which we can calculate from (30) and (35). For equation (30) we may write:

$$\left(\frac{b - b_0}{b_0} : \frac{b_k - b_0}{b_0}\right)^n = \frac{1 - \dfrac{b'_k}{x_k}\left(\dfrac{x}{x_k}\right)^n}{1 - b'_k : x_k},$$

i. e. with $(b_k - b_0) : b_0 = 2\gamma - 1$, $b'_k = (2\gamma - 1)^2 : 4\gamma(\gamma + 1)$,

$x_k = (2\gamma - 1) : (2\gamma + 1),\ x = (b - b_0) : (v - v_0)$:

$$\left(\frac{b - b_0}{b_0} \cdot \frac{1}{2\gamma - 1}\right) = \frac{1 - \dfrac{4\gamma^2 - 1}{4\gamma(\gamma+1)}\left(\dfrac{b - b_0}{v - v_0}\,\dfrac{2\gamma+1}{2\gamma-1}\right)^n}{1 - \dfrac{4\gamma^2 - 1}{4\gamma(\gamma+1)}} .$$

In this equation $b - b_0$ occurs both in the first and in the second member, and cannot be solved from it (in consequence of n^{th} power). We are therefore obliged to solve $v - v_0$ for the calculation, and then we find after some reductions ($v_0 = b_0$):

$$\frac{v - v_0}{v_0} = \frac{\dfrac{2\gamma+1}{2\gamma-1}\,\dfrac{b - b_0}{b_0}}{\sqrt[n]{\dfrac{4\gamma(\gamma+1)}{4\gamma^2 - 1} - \dfrac{4\gamma+1}{4\gamma^2 - 1}\left[\dfrac{1}{2\gamma - 1}\,\dfrac{b - b_0}{b_0}\right]^n}} , \quad . \quad . \quad (38)$$

in which $n = 8\gamma(\gamma+1) : (2\gamma - 1)(4\gamma + 1)$, $2\gamma - 1$ being $= 0{,}038 \sqrt{T}$.

In order to get an idea about the actual course of the curve $b = f(v)$ according to formula (38), I have taken the trouble — also with a view to testing the calculated values by those which the equation of state will yield for Argon e.g. — to calculate the corresponding values of $(b - b_0) : b_0$ and $(v - v_0) : v_0$ for different values of γ, i.e. of T.

The limiting value b_g for $v = \infty$ is evidently found by putting the denominator of (38) $= 0$, from which follows:

$$\frac{b_g - b_0}{b_0} = (2\gamma - 1) \sqrt[n]{\frac{4\gamma(\gamma+1)}{4\gamma + 1}} , \quad . \quad . \quad . \quad . \quad (38a)$$

agreeing with (34).

And with regard to the limiting value $(b - b_0) : (v - v_0)$ for $b = b_0$, $v = v_0$,

$$Lim\,\frac{(b - b_0)}{(v - v_0)} = x_0 = x_k \sqrt[n]{\frac{x_k}{b'_k}} = \frac{2\gamma - 1}{2\gamma + 1} \sqrt[n]{\frac{4\gamma(\gamma+1)}{4\gamma^2 - 1}} \qquad (38b)$$

follows immediately from (30b) of I, when instead of γ_k quite generally again γ is written.

a. $\gamma = 0{,}9$. ($T = \pm\, 450$ absolute).

For n we find $171 : 46 : 3{,}7174$, so that (38) etc. passes into

$$\left.\begin{array}{l} \dfrac{v - v_0}{v_0} = 3{,}5\,\dfrac{b - b_0}{b_0} : \sqrt[3,7]{\dfrac{171}{56} - \dfrac{115}{56}\left[\dfrac{5}{4}\,\dfrac{b - b_0}{b_0}\right]^{3,7}} \\ (b_g - b_0) : b_0 = 0{,}8 \sqrt[3,7]{171 : 115} \quad ; \quad x_0 = {}^2/_7 \sqrt[3,7]{171 : 56} \end{array}\right\} .$$

This yields the following survey (when for n not the shortened value 3,7, but 3,7174 is taken).

$$(b_g - b_0) : b_0 = 0{,}8901 \quad ; \quad x_0 = 0{,}3858$$

$(b-b_0):b_0=0.8$	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$(v-v_0):v_0=2.8:1$	2.45:	2.1:	1.75:	1.4:	1.05:	0.7:	0.35:
	1.1719	1.2582	1.3057	1.3313	1.3438	1.3488	1.3502
$=2.8$	2.091	1.669	1.340	1.052	0.781	0.519	0.259

Hence we have for $\gamma = 0{,}9$:

$b:b_0$	1.89	1.8	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1
$v:v_0$	∞	3.8*	3.09	2.67	2.34	2.05	1.78	1.52	1.26	1
$\frac{b-b_0}{v-v_0}$	0	0.286	0.335	0.360	0.373	0.380	0.384	0.385	0.386	0.386

It follows from this survey, what is of importance for practical purposes, that the direction of the curve $b=f(v)$ very soon — namely at about $v = 0{,}6\, v_{k'}$ — approaches the final direction given by $(b-b_0):(v-v_0) = 0{,}386$. I observed already in II p. 935 that since $b''_0 = 0$, the final part of the curve will have pretty much the *shape of a straight line*. This is actually the case; already for $v:v_0 = 2{,}34$, where $(b-b_0):(v-v_0) = 0{,}373$, the direction does not differ much from the final direction. We introduced just now the quantity $v_{k'}$ marked in this and the following tables by an *; by this is meant the value of v which *would* correspond with v_k, if the considered substance had its critical temperature at the assumed temperature (here ± 450°). Then namely $\gamma = 0{,}9 = \gamma_{k'}$, and hence $v_{k'} : v_0 = 2\,(\gamma_{k'} + 1) = 3{,}8$, so that $v = 2{,}34\, v_0$ is then $= 0{,}6\, v_{k'}$.

b. $\gamma = 0{,}75$. ($T = \pm\, 150$ absolute).

For n we find 5,25, and further:

$$\frac{v-v_0}{v_0} = 5\,\frac{b-b_0}{b_0} : \sqrt[5,25]{\frac{21}{5} - \frac{16}{5}\left(2\,\frac{b-b_0}{b_0}\right)^{5,25}} \,,$$

$$(b_g - b_0) : b_0 = 0{,}5\, \sqrt[5,25]{21:16} \quad ; \quad x_0 = 0{,}2\, \sqrt[5,25]{4{,}2}$$

giving:

$$(b_g - b_0) : b_0 = 0{,}5266 \quad ; \quad x_0 = 0{,}2629$$

$(b-b_0):b_0 = 0.5$	0.4	0.3	0.2	0.1
$(v-v_0):v_0 = 2.5:1$	2:	1.5:	1:	0.5:
	1.2486	1.3010	1.3128	1.3143
$= 2.5$	1.602	1.153	0.762	0.380

So we have for $\gamma = 0{,}75$:

$b:b_0$	1.53	1.5	1.4	1.3	1.2	1.1	1
$v:v_0$	∞	3.5*	2.60	2.15	1.76	1.38	1
$\frac{b-b_0}{v-v_0}$	0	0.200	0.250	0.260	0.262^5	0.263	0.263

Here too the curve $b = f(v)$ is almost rectilinear for $v = 0{,}6\, v_{k'}$, nay even for $v = 2{,}6\, v_0 = 0{,}75\, v_{k'}$.

Just as for $\gamma = 0{,}9$ we see also clearly in the above table, *that the greatest change of b will be in the neighbourhood of the critical (or pseudo-critical) point*; hence the comparatively large values of b'_k and b''_k, through which $r = v_k : b_k$ is reduced from the ideal value 3 to a much lower value, e.g. 2,1 (for $\gamma_k = 0{,}9$) or 2,33 (for $\gamma_k = 0{,}75$). We may say that the curve $b = f(v)$ at the beginning and at the end runs almost rectilinearly (at the beginning, between $v = \infty$ and $v =$ somewhat $> v_k$, parallel to the v-axis), while in the part somewhat before and somewhat past v_k the change of direction takes place from 0 to the final direction given by x_0 (above resp. 0,39 and 0,26).

c. $\underline{\gamma = 0{,}70}$. ($T = \pm\, 100$).

Now $n = 119 : 19 = 6{,}2632$, and further:

$$\frac{v - v_0}{v_0} = 6\, \frac{b - b_0}{b_0} : \left\{ \sqrt[6,26]{\frac{119}{24} - \frac{95}{24}\left(2{,}5\, \frac{b - b_0}{b_0}\right)^{6,26}} \right\},$$

$$(b_g - b_0) : b_0 = 0{,}4 \sqrt[6,26]{119 : 95} \quad ; \quad x_0 = {}^1/_6 \sqrt[6,26]{119 : 24}$$

from which follows:

$$(b_g - b_0 : b_0 = 0{,}4146 \quad ; \quad x_0 = 0{,}2152$$

$(b-b_0):b_0 = 0.4$	0.3	0.2	0.1
$(v-v_0):v_0 = 2.4:1$	1.8 : 1.2625	1.2 : 1.2891	1.1 : 1.2912
$= 2.4$	1.426	0.931	0.465

In consequence of this we have for $\gamma = 0{,}70$:

$b:b_0$	1.41^5	1.4	1.3	1.2	1.1	1
$v:v_0$	∞	3.4*	2.43	1.93	1.46^5	1
$\dfrac{b-b_0}{v-v_0}$	0	0.167	0.210	0.215	0.215	0.215

For $v:v_0 = 2{,}43$, hence $v = 0{,}7\, v_{k'}$, the final direction has already been reached.

d. $\underline{\gamma = 0{,}65}$. $(T = \pm 50)$.

For n we find the value $143:18 = 7{,}9444$. Further:

$$\left.\begin{array}{c}\dfrac{v-v_0}{v_0} = \dfrac{23}{3}\,\dfrac{b-b_0}{b_0} : \sqrt[7,9]{\dfrac{143}{23} - \dfrac{120}{23}\left(\dfrac{10}{3}\,\dfrac{b-b_0}{b_0}\right)^{7,9}} \\ (b_g - b_0):b_0 = 0{,}3\,\sqrt[7,9]{143:120} \quad ; \quad x_0 = {}^3/_{23}\,\sqrt[7,9]{143:23}\end{array}\right\},$$

giving:

$$(b_g - b_0):b = 0{,}3067 \quad ; \quad x_0 = 0{,}1642$$

$(b-b_0):b_0 = 0.3$	0.2	0.1
$(v-v_0):v_0 = 2.3:1$	$^{23}/_{15}$: 1.2532	$^{23}/_{30}$: 1.2586
$= 2.3$	1.223^5	0.609

Hence we have for $\gamma = 0{,}65$:

$b:b_0$	1.31	1.3	1.2	1.1	1
$v:v_0$	∞	3.3*	2.22	1.61	1
$(b-b_0):(v-v_0)$	0	0.130	0.163^5	0.164	0.164

The final direction is again reached for $v = 0{,}7\, v_{k'}$.

e. $\underline{\gamma = 0{,}60}$. ($T = \pm 25$).

The value of n is $192 : 17 = 11{,}294$. In consequence of this:

$$\left.\begin{array}{l} \dfrac{v-v_0}{v_0} = 11\, \dfrac{b-b_0}{b_0} : \sqrt[11,3]{\dfrac{96}{11} - \dfrac{85}{11}\left(5\, \dfrac{b-b_0}{b_0}\right)^{11,3}} \\ (b_g - b_0) : b_0 = 0{,}2\, \sqrt[11,3]{96 : 85} \quad ; \quad x_0 = {}^1/_{11}\, \sqrt[11,3]{96 : 11} \end{array}\right\},$$

giving:

$$(b_g - b_0) : b_0 = 0{,}2022 \quad ; \quad x_0 = 0{,}1101$$

$(b-b_0) : b_0 = 0.2$	0.1
$(v-v_0) : v_0 = 2.2 : 1 = 2.2$	$1.1 : 1.2114 = 0.908$

so that for $\gamma = 0{,}60$:

$b : b_0$	1.202	1.2	1.1	1
$v : v_0$	∞	3.2*	1.91	1
$(b-b_0) : (v-v_0)$	0	0.091	0.110	0.110

A little beyond $v_{k'}$ the deviation of the final direction is already unimportant.

f. $\underline{\gamma = 0{,}55}$. ($T = \pm 5$).

Here n is $= 341 : 16 = 21{,}3125$, and further:

$$\left.\begin{array}{l} \dfrac{v-v_0}{v_0} = 21\, \dfrac{b-b_0}{b_0} : \sqrt[21,3]{\dfrac{341}{21} - \dfrac{320}{21}\left(10\, \dfrac{b-b_0}{b_0}\right)^{21,3}} \\ (b_g - b_0) : b_0 = 0{,}1\, \sqrt[21,3]{341 : 320} \quad ; \quad x_0 = {}^1/_{21}\, \sqrt[21,3]{341 : 21} \end{array}\right\},$$

from which follows:

$$(b_g - b_0) : b_0 = 0{,}1003 \quad ; \quad x_0 = 0{,}05428,$$

so that we find (e.g. for a *Helium* isotherm at its critical temperature):

$b : b_0$	1.1003	1.1	1
$v : v_0$	∞	3.1*	1
$(b-b_0) : (v-v_0)$	0	0.0476	0.0543

And finally for $\gamma = 0{,}50$ ($T = 0$), where b is invariable, we should find $b : b_0 = 1$ for all values of $v : v_0$, $(b - b_0) : (v - v_0)$ always being $= 0$.

Let us in conclusion review according to what law or approximate law the found value of x_0 — i. e. of the final direction of the curve $b = f(v)$ — varies with γ or T.

From (38*b*) follows $x_0 = (2\gamma - 1) \times \frac{1}{2\gamma + 1} \sqrt[n]{\frac{4\gamma(\gamma + 1)}{4\gamma^2 - 1}}$. We shall see that here the factor of $2\gamma - 1$ is almost constant between $\gamma = 0{,}75$ and $\gamma = 0{,}55$.

$\gamma = 0.90$	0.75	0.70	0.65	0.60	0.55	0.50
$x_0 = 0.386$	0.263	0.215	0.164	0.110	0.0543	0
$x_0 : (2\gamma - 1) = 0.482$	0.526	0.538	0.547	0.551	0.543	0.5

If 0,482 for $\gamma = 0{,}9$ and 0,5 for $\gamma = 0{,}5$ is excepted, the mean value of the other values is 0,541, and we may therefore write with some accuracy:

$$Lim \left(\frac{b - b_0}{v - v_0}\right)_0 = 0{,}54\,(2\gamma - 1).$$

But seeing that $2\gamma - 1 = 0{,}038\sqrt{T}$, we have also:

$$Lim \frac{b - b_0}{v - v_0} = 0{,}02\sqrt{T}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

which according to the above will therefore also hold *all along the final part* of the curve $b = f(v)$, from values of $v = 0{,}7\,v_k$ to $v = v_0$.

For Argon at temperatures $\leqq T_k$ only $\gamma = 0{,}75$ ($T = 150$) and $\gamma = 0{,}70$ ($T = 100$) should practically be taken into account, because the observations have not been carried further than $T = 90$ (absolute). If we thus consider an isotherm for Argon below the critical point, we may assume that (provided it be not *too* near T_k) the value of b will practically agree with b_g at the *vapour* volume, and that at the *liquid* volume the b-value will satisfy the above equation (39).

If (39) is written in the reduced form

$$Lim \frac{(b : v_k) - (v_0 : v_k)}{(v : v_k) - (v_0 : v_k)} = 0{,}02\sqrt{T},$$

and if it is taken into account that $b : v_k = \beta$, $v : v_k = n$, and $v_0 : v_k = n_0 = \beta_0 = 1 : 2\,(1 + \gamma_k)$, then for Argon:

$$(\beta - {}^2/_7) : (n - {}^2/_7) = 0{,}02\sqrt{T}, \qquad (n < 0{,}7) \quad . \quad . \quad (40)$$

when $\gamma_k = 0{,}75$ is taken.

As $1-(\beta-{}^2/_7):(n-{}^2/_7)$ also $=(n-\beta):(n-{}^2/_7)$, we may also write:

$$n-\beta=(n-{}^2/_7)(1-0{,}02\sqrt{T})\,,\qquad (n<0{,}7)\quad .\quad .\quad (40a)$$

in which $n-\beta$ is determined by the equation of state (37). Equation (40^a) may serve among others to determine the dependence of the reduced liquid volume on the temperature at low temperatures.

17. *Calculation of the b-values from the isotherms of Argon.*

In order to be able to draw up the reduced equation of state of Argon, we must in the first place accurately know the critical data. For the critical density ϱ_k I took the value 0,53078 from Comm. Leiden 131 (Mathias, Kamerlingh Onnes and Crommelin). Abbreviated therefore 0,531. In this it is assumed that the straight diameter remains straight up to the critical point. The values of Crommelin in Comm. 115 ($\varrho_k=0{,}509$) and Comm. 118^a ($\varrho_k=0{,}496$) are both too low.

For T_k has been taken $-122°{,}44$ C $=150{,}65$ absolute, and for p_k the value 47,996, shortened to 48,0 — both from Comm. 115.

For s we assumed the value $s=3{,}424$ from Comm. 131. In Comm. $120a$ (Kamerlingh Onnes and Crommelin) a too low value, viz. 3,283, has been given (in connection with the too slight critical density).

At last the value of f. We derive from Comm. 120^a $f>2{,}577\times\times 2{,}3026$, hence $f>5{,}933$. (Comm. 115 gives the too low value 5,712). From $s=8f':(8+f')$ — see I, formula (7) — would follow $f'=5{,}986$. And from $f'=8\gamma$ — see I, formula (17) — follows with $\gamma=0{,}7446$ the value $f'=5{,}957$. Now $f=f'(1+\varphi)$ — see I, formula (5) — hence, as φ is small positive, f *slightly* greater than f'. We may therefore safely conclude to the value 6,00 for f from the two values 5,99 and 5,96 for f', which also fulfils the condition $f>5{,}93$.

Comm. 131 gives $0{,}0026235\;T_k:\varrho_k$ as reduced coefficient of direction for the straight diameter, giving with the above given values of T_k and ϱ_k the value $\gamma=0{,}7446$. We saw just now that this value yields a good value for f'. From $s=8\gamma:(1+\gamma)$ would follow $\gamma=0{,}748$ for γ. The former value from Comm. $120a$, viz. $0{,}003050\;T_k:\varrho_k=0{,}9027$, is much too high, and would be quite in contradiction with our temperature-relation $2\gamma-1=0{,}038\sqrt{T}$, which yields 0,738, in good harmony with 0,745, but not in harmony with 0,903, which high value of γ would belong to substances of the Isopentane type with a critical temperature of about 450 absolute, i.e. three times as high as that of Argon.

We see from this how useful the above table in § 15, in conjunction with that in I, p. 819, can be for a first orientation concerning the critical data.

Now the equation of state (37) passes into (assuming the value 6 also for f')

$$\left(\varepsilon+\frac{5}{n^2}\right)(n-\beta)=3{,}424\ m,$$

from which may be solved.

$$\beta=n-\frac{3{,}424m}{\varepsilon+5:n^2}\ .$$

The following values have all been derived from Comm. 118*b*, p. 19 et seq. (Kamerlingh Onnes and Crommelin) and from these Proceedings of Oct. 1913 p. 477 et seq. (Crommelin). (See also Comm. 138).

The value β_k follows from $r=v_k:b_k=1:\beta_k$, hence $\beta_k=1:r$. Now $r=(1+\gamma):\gamma$ — see I, formula (14) — so that $\beta_k=\gamma:(1+\gamma)=0{,}427$. With $r=1+8:f'$ (see I, (7)) follows with $f'=6$ for r the value 2,33, hence for β_k the value $^3/_7=0{,}429$. As further $2\gamma=b_k:b_0=$ $=\beta_k:\beta_0$, we have $\beta_0=\beta_k:2\gamma=0{,}429:1{,}5=0{,}286$.

We are not yet ready to carry out the calculations, as the given volumes must all be changed into "reduced" volumes. Now $\varrho=0{,}1073$ corresponds with $d_A=60{,}21$, (Comm. 118, p. 8), so $\varrho=0{,}5308$ (the critical density, corresponding to $n=1$) would correspond to $d_A=297{,}84$, i. e. to $V_A=1:297{,}84$. This is therefore the value of V_A at the critical point. To reduce this to 1 ($n=1$), this and all the other volumes must be multiplied by the factor 297,84.

a. The isotherm of 20°,39 C, i. e. (with $T_0=273{,}09$) $T=293{,}48$ absolute. From this follows $m=293{,}48:150{,}65=1{,}948$, so $3{,}424\ m=$ $=6{,}670$, so that

$$n-\beta=6{,}670:(\varepsilon+5:n^2).$$

Now e. g. $d_A=20{,}499$ has been given (for $p=21{,}783$). So the value V_A is $1:20{,}499$, hence according to the above $n=297{,}84:20{,}499$. We must therefore divide 297,84 by all the given values of d_A. Thus we calculate the following survey.

p	d_A	ε	n	$\varepsilon+5:n^2$	$n-\beta$	β
21.783	20.499	0.4538	14.529	0.4775	13.969	0.560
34.487	32.590	0.7185	9.139	0.7784	8.570	0.569
49.604	47.319	1.0334	6.294	1.1597	5.752	0.542
61.741	59.250	1.2863	5.027	1.4842	4.494	0.532
					Mean	0.551

From (35) with $\sqrt{T} = \sqrt{293,5} = 17,13$ would follow $\gamma = 0,825$, referring to a substance which would have its critical temperature at 293,5. Then (see above) $\beta_{k'}$ would be $= \beta_0 \times 2\gamma = 0,471$, while $\beta_g = \beta_0 \times 1,708$ would be $= 0,488$. [See *a.* and *b.* of § 16; 1,708 for $\gamma = 0,825$ is the mean value of 1,8901 for $\gamma = 0,9$ and 1,5266 for $\gamma = 0,75$].

The above found values of β (which will probably practically agree with β_g) are all higher than the value of β_g calculated from our formula.

b. The isotherm of $\underline{-57°,72}$; i. e. $T = 215,37$, $m = \underline{1,430}$, and so $3,424\,m = 4,895$. From $n - \beta = 4,895 : (\varepsilon + 5 : n^2)$ the following table is calculated.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
17.872	23.509	0.3723	12.669	0.4035	12.131	0.538
35.127	48.116	0.7318	6.190	0.8623	5.677	0.513
46.209	64.948	0.9627	4.586	1.2005	4.078	0.508
62.079	90.695	1.2933	3.284	1.7569	2.786	0.498
					Mean	0.514

Just as above we can again fix the limits of β, corresponding to a temperature of 215 absolute. With $\sqrt{T} = 14,68$ corresponds $\gamma = 0,779$; hence $\beta_{k'} = 0,445$, $\beta_g = \beta_0 \times 1,597 = 0,456$. Again β, calculated from the equation of state, is higher than the value calculated from our formula.

c. Isotherm of $\underline{-102°,51} = 170,58$ absolute. Then $m : \underline{1,132}$, hence $3,424\,m = 3,8770$.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
14.864	25.571	0.3097	11.648	0.3466	11.188	0.460
32.394	62.240	0.6749	4.785	0.8932	4.340	0.445
40.976	84.002	0.8537	3.546	1.2513	3.099	0.447
51.398	115.88	1.0708	2.570	1.8276	2.121	0.449
62.239	158.01	1.2967	1.885	2.6938	1.434	0.451
					Mean	0.450

With $T = 170,6$ corresponds $\gamma = 0,748$, $\beta_{k'} = 0,427$, $\beta_g = \beta_0 \times 1,522 =$

$= 0{,}435$. The β-values from the equation of state are still somewhat too high.

d. The isotherm of $-116°{,}62 = 156{,}47$ absolute. This yields $m = 1{,}039$, hence $3{,}424\,m = 3{,}556$.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
13.863	26.480	0.2888	11.248	0.3287	10.824	0.424
37.250	90.563	0.7760	3.289	1.2429	2.867	0.422
50.259	159.71	1.0471	1.865	2.4992	1.427	0.438
54.922	210.02	1.1442	1.418	3.6551	0.976	0.442
60.669	331.29	1.2639	0.8990	7.5120	0.475	0.424
					Mean	0.430

With $T = 156{,}5$ corresponds $\gamma = 0{,}738$, yielding $\beta_{k'} = 0{,}422$, $\beta_g = \beta_0 \times 1{,}500 = 0{,}429$. As, just as in the above tables, $n > 1$ (the last value is a little smaller), no appreciable diminution of the limiting value β_g can be expected for β yet. Now that we approach the critical temperature of Argon, however, the mean value 0,48 found in the table (calculated from the equation of state) agrees with the theoretical value of β_g which can be calculated from our formula.

e. The isotherm of $-121°{,}21 = 151{,}88$ absolute, so slightly above the critical temperature. Here $m = 1{,}008$, hence $3{,}424\,m$ becomes $= 3{,}452$.

p	d_A	ε	n	$\varepsilon + 5 : n^2$	$n - \beta$	β
13.754	27.326	0.2865	10.899	0.3290	10.497	0.402
30.122	71.459	0.6275	4.168	0.9183	3.765	0.403
37.465	100.33	0.7805	2.969	1.3536	2.556	0.413
45.282	148.95	0.9434	2.000	2.2064	1.569	0.431
49.865	234.13	1.0389	1.272	4.1596	0.833	0.439
50.885	333.75	1.0601	0.8924	7.4013	0.468	0.424
					Mean	0.419

With $T = 151{,}88$ corresponds $\gamma = 0{,}734$, $\beta_{k'} = 0{,}419$, $\beta_g = \beta_0 \times \times 1{,}491 = 0{,}426$. The found mean value, though slightly too small, agrees pretty well with it.

Fontanivent sur Clarens, March 1914.

(*To be concluded*).

Chemistry. — *"The reciprocal pairs of salts $KCl + NaNO_3 \rightleftarrows NaCl + KNO_3$ and the manufacture of conversion salpetre."* By Prof. W. REINDERS. (Communicated by Prof. F. A. H. SCHREINEMAKERS.)

(Communicated in the meeting of February 28, 1914).

As is well known we understand by two reciprocal pairs of salts, the two pairs that can be built up from two different cations and two different anions and can be converted into each other by double decomposition.

The instance of this mostly quoted is the system:

$$KCl + NaNO_3 \rightleftarrows KNO_3 + NaCl,$$

known by the technical application of this transformation in the manufacture of conversion salpetre.

Notwithstanding the technical importance of this system, a systematic research as to the equilibria occurring therein was still wanting.

Hence was started in 1909 by Miss J. PH. VAN REES and myself a research of this kind, which on account of the departure of the first named could not be continued, but has since been completed in cooperation with Mr. R. DE LANGE. The results of these researches will be communicated here briefly.

Meanwhile appeared in 1910 the publication of an investigation of these equilibria at 25° by KENJIRO UYEDA [1]), to which our attention was called by a communication thereon by E. JÄNECKE [2]). His figures agree very well with our determinations at 25°. Besides at 25°, we have determined the equilibrium also at 5°, 50°, and 100°.

We will indicate the composition of the solutions in the manner proposed by E. JÄNECKE [3]) according to the scheme:

$$xK, \quad (1-x)Na, \quad yNO_3, \quad (1-y)Cl, \quad mH_2O$$

in which m is, therefore, the number of grm. mols. of water in which 1 grm. mol. of salt is dissolved.

The graphic representation of the different solutions then becomes a figure in space having as ground plane a quadrangle of the side $=1$ of which two sides coincide with the x and the y-axis. The four salts then form the apexes of this quadrangle, mixtures of two salts with homonymous ions are placed at the borders of this quadrangle

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[1]) Memoirs of the College of Science and Engineering, Kyoto Imperial University 1909/1910 II, 245—251.

[2]) Zeitschr. f. anorg. Chem. **71**, 1 (1911).

[3]) Zeitschr. f. anorg. Chem. **51**, 132 (1908); **71**, 1 (1911).

and mixtures containing all four ions are represented by a point within the quadrangle. If now, in the point indicating the proportion of salts in the solution, we erect a perpendicular line of the length m, the composition of this solution will then be fully determined by the terminal point of the perpendicular line.

The equilibria at 25°.

The solutions saturated with one or more of the solid salts are indicated in table I.

Fig. 1 is the horizontal projection of the spacial figure.

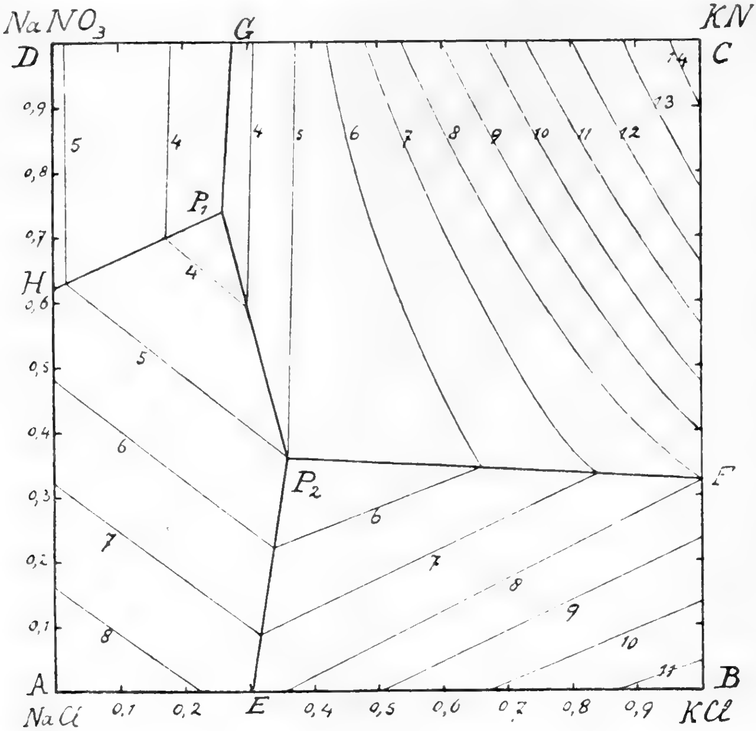

Fig. 1.

In addition to the lines indicating the equilibrium with two solid salts are also projected therein the *isohydores*, the lines that unite saturated solutions with equal water contents.

In this figure are encompassed by the lines

AEP_2P_1HA the region of solutions in equilibrium with solid NaCl
$EBFP_2E$,, ,, ,, ,, ,, ,, ,, solid KCl
FP_2P_1GCF ,, ,, ,, ,, ,, ,, ,, solid KNO_3
DGP_1HD ,, ,, ,, ,, ,, ,, ,, solid $NaNO_3$

TABLE I. Solubility at 25°.

N°.	Grms. of salt in 100 grms. of water.				Solid salt in equilibrium with the solution.	Sol.: xK, $(1-x)$ Na, yNO$_3$ $(1-y)$ Cl, m H$_2$O.		
	NaCl	KCl	NaNO$_3$	KNO$_3$		xK	yNO$_3$	mH$_2$O
A	36.04	—	—	—	NaCl	0	0	9.01
	34.13	5	—	—	»	0.103	0	8.53
	32.28	10	—	—	»	0.195	0	8.09
	30.27	15	—	—	»	0.280	0	7.72
E	29.62	16.45	—	—	NaCl + KCl	0.303	0	7.63
	20	21.68	—	—	KCl	0.459	0	8.77
	15	24.66	—	—	»	0.563	0	9.45
	12	26.78	—	—	»	0.636	0	9.84
B	0	35.98	—	—	»	1.00	0	11.51
	0	35.80	—	5	»	1.00	0.093	10.48
	—	35.54	—	10	»	1.00	0.172	9.64
	—	35.12	—	15	»	1.00	0.240	8.96
F	—	34.92	—	22.79	KCl + KNO$_3$	1.00	0.325	8.00
	—	15	—	28.93	KNO$_3$	1.00	0.599	11.39
	—	10	—	31.49	»	1.00	0.699	12.46
	—	5	—	34.89	»	1.00	0.838	13.44
C	—	0	—	38.85	»	1.00	1.00	14.65
	—	—	5	37.96	»	0.865	1.00	12.78
	—	—	10	37.49	»	0.759	1.00	11.37
	—	—	15	37.42	»	0.677	1.00	10.15
	—	—	20	37.54	»	0.612	1.00	9.15
	—	—	40	39.39	»	0.453	1.00	6.48
	—	—	60	41.87	»	0.370	1.00	4.95
G	—	—	100.90	46.15	KNO$_3$ + NaNO$_3$	0.278	1.00	3.38
	—	—	97.95	30	NaNO$_3$	0.205	1.00	3.83
	—	—	96.06	20	»	0.149	1.00	4.18
	—	—	94.47	10	»	0.082	1.00	4.62
	—	—	93.39	5	»	0.042	1.00	4.83
D	—	—	91.86	0	»	0	1.00	5.14
	5	—	84.67	—	»	0	0.921	5.13
	10	—	77.46	—	»	0	0.842	5.13
	15	—	70.69	—	»	0	0.764	5.10
H	23.62	—	58.01	—	NaNO$_3$ + NaCl	0	0.624	5.08
	32.87	—	15	—	NaCl	0	0.239	7.51
	33.90	—	10	—	»	0	0.169	7.96
	35.07	—	5	—	»	0	0.089	8.43
A	36.04	—	—	—	»	0	0	9.01
	24.82	22.2	15.4	—	NaCl + KCl	0.33	0.20	6.15
	21.36	20.00	—	32.9	KCl + KNO$_3$	0.62	0.34	5.79
	24.5	—	61.3	17.2	KNO$_3$ + NaNO$_3$	0.13	0.68	4.24
	7.0	—	82.1	43.15	NaNO$_3$ + NaCl	0.27	0.88	3.51
P$_1$	23.8	—	64.0	41.2	NaCl + NaNO$_3$ + KNO$_3$	0.26	0.74	3.54
P$_2$	41.5	—	—	40.3	NaCl + KCl + KNO$_3$	0.36	0.36	5.01

The lines of demarcation between these planes: EP_2, FP_2, GP_1, HP_1 and P_1P_2 indicate the solutions which are in equilibrium with two solid salts, and the points P_1 and P_2 the solutions saturated with three solid salts.

We notice there are no solutions saturated with both KCl and $NaNO_3$. This pair of salts is, therefore the *unstable* pair. If to a solid mixture of these salts we add a little water a solution will form in which one of the salts disappears and solid KNO_3, solid NaCl or both these solid phases are formed.

NaCl and KNO_3 are the *stable* pair and the line P_1P_2 indicates the solutions saturated with these salts.

The point P_1 which represents the solution saturated with the three solid salts NaCl, $NaNO_3$ and KNO_3 lies entirely within the triangle, whose points indicate the composition of these salts. The solution is, therefore "congruent-saturated". P_2 lies just on the diagonal NaCl—KNO_3. Hence, this solution is still just "congruent-saturated".

The equilibrium at 5°, 50°, *and* 100°.

The result of the determinations at these temperatures is contained in the tables 2, 3, and 4. In fig. 2 these equilibria are represented graphically.

TABLE 2. Solubility at 5° C.

N⁰.	Grms. of salt in 100 grms. of water.				Solid salt in equilibrium with the solution.	Sol.: $xK, (1-x) Na, yNO_3, (1-y) Cl, mH_2O$.		
	NaCl	KCl	$NaNO_3$	KNO_3		xK	yNO_3	mH_2O
A	35.74	—	—	—	NaCl	0	0	9.09
E	31.50	10.40	—	—	NaCl + KCl	0.207	0	8.19
	13.93	20.01	—	—	KCl	0.53	0	10.96
B	—	29.76	—	—	KCl	1.00	0	13.91
F	—	29.87	—	10.14	KCl + KNO_8	1.00	0.20	11.07
	—	16.32	—	11.40	KNO_3	1.00	0.34	16.74
C	—	—	—	16.83	KNO_3	1.00	1.00	33.34
	—	—	22.30	15.57	KNO_3	0.37	1.00	13.34
G	—	—	82.10	18.1	$KNO_3 + NaNO_3$	0.155	1.00	4.80
D	—	—	76.3	—	$NaNO_3$	0	1.00	6.19
	19.42	—	50.1	—	$NaNO_3$	0	0.64	6.03
H	27.6	—	41.7	—	$NaNO_3$ + NaCl	0	0.51	5.77
	35.1	5.16	—	10.1	NaCl + KCl	0.22	0.13	7.21
	19.5	13.65	—	13.88	KCl + KNO_3	0.49	0.21	8.49
	22.0	—	56.0	14.26	$KNO_3 + NaNO_3$	0.12	0.68	4.72
	27.5	—	42.5	3.03	$NaNO_3$ + NaCl	0.03	0.53	5.55
P_1	29.1	—	44.3	14.0	NaCl, $NaNO_3$, KNO_3	0.12	0.57	4.80
P_2	38.5	0.64	—	20.7	NaCl, KCl, KNO_3	0.23	0.22	6.50

TABLE 3. Solubility at 50° C.

N⁰.	Grms. of salt in 100 grms. of water.				Solid salt in equilibrium with the solution.	Sol.: xK, $(1-x)$ Na, $y NO_3$, $(1-y)$ Cl, $m H_2O$.		
	NaCl	KCl	$NaNO_3$	KNO_3		xK	$y NO_3$	$m H_2O$
A	36.72	—	—	—	NaCl	0	0	8.85
E	28.35	23.09	—	—	NaCl + KCl	0.39	0	6.99
	15.96	29.24	—	—	KCl	0.59	0	8.35
B	—	42.80	—	—	„	1.00	0	9.67
	—	41.39	—	24.05	„	1.00	0.30	7.00
F	—	38.75	—	52.54	KCl + KNO_3	1.00	0.50	5.34
C	—	—	—	85.10	KNO_3	1.00	1.00	6.60
	—	—	57.89	87.53	„	0.56	1.00	3.59
G	—	—	134.9	90.2	KNO_3 + $NaNO_3$	0.36	1.00	2.24
D	—	—	114.1	—	$NaNO_3$	0	1.00	4.14
H	20.5	—	84.8	—	$NaNO_3$ + NaCl	0	0.74	4.12
	28.4	—	43.9	—	NaCl	0	0.51	5.61
	34.0	13.4	—	24.3	NaCl + KCl	0.42	0.24	5.55
	12.7	25.4	—	58.6	KCl + KNO_3	0.81	0.51	4.88
	19.2	—	104.1	27.7	NaCl + $NaNO_3$	0.15	0.82	3.04
P_1	12.2	—	110.7	82.2	NaCl, $NaNO_3$, KNO_3	0.35	0.91	2.39
P_2	59.9	—	6.1	70.9	NaCl, KCl. KNO_3	0.48	0.53	3.80

TABLE 4. Solubility at 100°.

N⁰.	Grms. of salt in 100 grms. of water.				Solid salt in equilibrium with the solution.	Sol.: xK, $(1-x)$ Na, $y NO_3$, $(1-y)$ Cl, $m H_2O$.		
	NaCl	KCl	$NaNO_3$	KNO_3		xK	$y NO_3$	$m H_2O$
A	39.2	—	—	—	NaCl	0	0	8.29
E	27.3	36.2	—	—	NaCl + KCl	0.51	0	5.83
B	—	56.0	—	—	KCl	1.00	0	7.38
F	—	41.6	—	199.0	KCl + KNO_3	1.00	0.78	2.20
C	—	—	—	246	KNO_3	1.00	1.00	2.28
G	—	—	233.6	218.0	KNO_3 + $NaNO_3$	0.44	1.00	1.13
D	—	—	176	—	$NaNO_3$	0	1.00	2.68
H	19.2	—	158.0	—	$NaNO_3$ + NaCl	0	0.85	2.54
P_1	6.5	—	207.5	194.6	NaCl, $NaNO_3$, KNO_3	0.43	0.975	1.24
P_2	35.9	—	47.0	192.2	NaCl, KCl, KNO_3	0.62	0.80	1.81

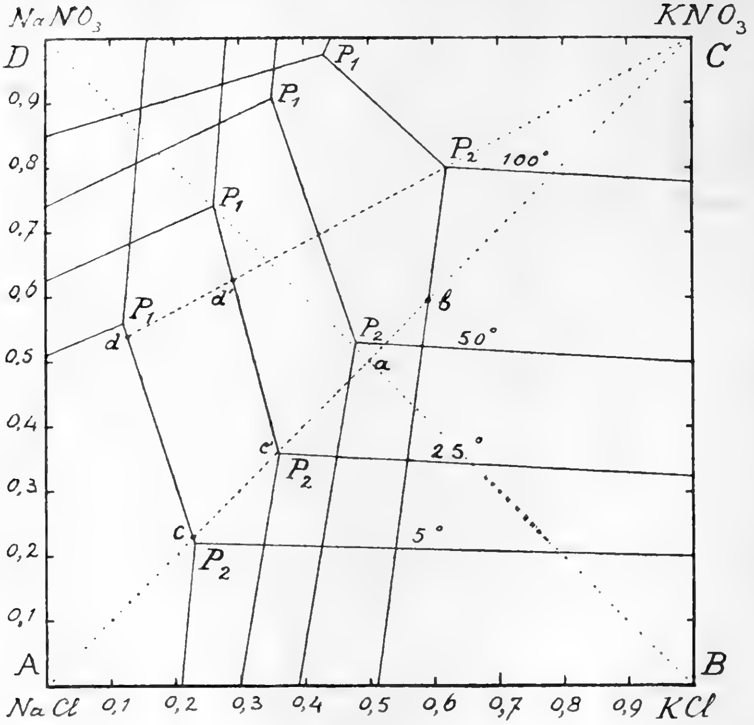

Fig. 2.

The general character of the equilibrium line is not influenced by the change in temperature. It appears, however, that at an elevation of temperature the region of NaCl becomes much larger and that of KNO_3 and $NaNO_3$ much smaller. Hence, P_1 and P_2 shift considerably upwards.

P_1 always remains congruent saturated, P_2 is so also at 5°; at 50° and 100°, however it lies outside the triangle NaCl, KCl, KNO_3 and the solution is no longer congruent saturated. A solution is formed with separation of solid KCl when NaCl and KNO_3 are treated with water.

It further appears that at all temperatures the solubility of $NaNO_3$ (per 100 grams of water) is not lowered by addition of KNO_3, as might be expected from a salt with a homonymous ion on the ground of the theory of electrolytic dissociation, but increased. At a high temperature this behaviour is comprehensible, if we consider that the eutecticum of the system $NaNO_3$—KNO_3 lies at 218°. The solubility of the eutectic mixture (49 mol. % $NaNO_3$ to 51 mol. % KNO_3) is then $= \infty$ whereas the solubility of $NaNO_3$ and KNO_3 at the temperature of 218° will still have definite values. As this eutecticum forms the terminus of the line indicating the change of the point G with the temperature, the solution G, at temperatures somewhat below the eutecticum will contain less water than the solutions of pure $NaNO_3$ or KNO_3 saturated at the same temperature.

UYEDA's idea that the increased solubility of $NaNO_3$ by addition of KNO_3 would point to the formation of a double salt in solution is, therefore, not confirmed.

Application to the conversion process.

Let us now see how from the figures obtained may be deduced the most appropriate process for the preparation of potash salpetre and let us calculate the yield of the conversion in the following methods of working.

I. KCl and $NaNO_3$ are mixed in equimolecular quantities (say, half a gram. mol. of each), dissolved in water and the liquid evaporated at 100° isotherm. When the water content of the liquid has sunk to $m = 3{,}5$ (point a in fig. 2) solid NaCl begins to deposit. The composition of the liquid now changes in the direction ab. At b (point of intersection with the line FP_2) the solution is also saturated with KCl. A further evaporation would then cause KCl to deposit as wel as NaCl so that the liquid would change its composition in the direction bP_2 (100°). As we only wish to separate NaCl, the water content may, therefore, not fall below that of solution b. The solution b has the composition:

$$0{,}59 \text{ K} \;,\; 0{,}41 \text{ Na} \;,\; 0{,}59 \text{ NO}_3 \;,\; 0{,}41 \text{ Cl} \;,\; 2{,}83 \text{ H}_2\text{O} \,.$$

The change of liquid a ($0{,}5\ NaNO_3$, $0{,}5\ KCl$, $3{,}50\ HO_2$) to liquid b and solid NaCl has then taken place according to the following equation:

$$\underset{(a)}{\left\{\begin{array}{l} 0{,}5\text{ Na}\ \ 0{,}5\text{ K} \\ 0{,}5\text{ Cl}\ 0{,}5\text{ NO}_3 \\ 3{,}50\text{ H}_2\text{O} \end{array}\right\}} = 0{,}153\text{ NaCl} + 1{,}10\text{ H}_2\text{O} + \frac{50}{59}\underset{(b)}{\left\{\begin{array}{l} 0{,}59\text{ KNO}_3 \\ 0{,}41\text{ NaCl} \\ 2{,}83\text{ H}_2\text{O} \end{array}\right\}}$$

Let us now imagine the solution b separated from the solid sodium chloride and cooled to 5°.

This solution lies in the diagram for 5° in the region of KNO_3. It is strongly supersaturated with KNO_3 and will allow this to crystallise. Its composition then changes in the direction bac. The most extreme solution attainable without depositing solid NaCl is the solution c, the composition of which is $0{,}235\ KNO_3$, $0{,}765$ NaCl, $6{,}40\ H_2O$.

As a rule, however, in order to attain this solution, a withdrawal or addition of water will be necessary in addition to a withdrawal of KNO_3. The general equation thus becomes:

$$\left\{\begin{array}{ll} 0{,}59 & KNO_3 \\ 0{,}41 & NaCl \\ 2{,}83 & H_2O \end{array}\right\} = x\ H_2O + y\ KNO_3 + z \left\{\begin{array}{ll} 0{,}235 & KNO_3 \\ 0{,}765 & NaCl \\ 6{,}40 & H_2O \end{array}\right\}$$

If from this we calculate the values x, y, and z, we find

$$x = -0{,}600 \qquad y = 0{,}464 \qquad z = 0{,}536.$$

x is negative, that is to say that to the liquid b must be added water so as to prevent the point c to be surpassed. If this is not done NaCl will deposit as well as KNO_3 and the salpetre obtained will be impure.

In a continuous process the liquid obtained, c, will be again converted into the solution b by addition of fresh $NaNO_3$ and KCl in which case separation of NaCl takes place.

The transformations of b to c at 5° and from c to b at 100° now take place according to the subjoined equations:

$$\left\{\begin{array}{ll} 0{,}59 & KNO_3 \\ 0{,}41 & NaCl \\ 2{,}83 & H_2O \end{array}\right\} + 0{,}600\ H_2O = 0{,}464\ KNO_3 + 0{,}536 \left\{\begin{array}{ll} 0{,}235 & KNO_3 \\ 0{,}765 & NaCl \\ 6{,}40 & H_2O \end{array}\right\}$$

and

$$0{,}536 \left\{\begin{array}{ll} 0{,}235 & KNO_3 \\ 0{,}765 & NaCl \\ 6{,}40 & H_2O \end{array}\right\} + 0{,}464\ KCl + 0{,}464\ NaNO_3 = \left\{\begin{array}{ll} 0{,}59 & KNO_3 \\ 0{,}41 & NaCl \\ 2{,}83 & H_2O \end{array}\right\} +$$

$$+\ 0{,}464\ NaCl + 0{,}600\ H_2O.$$

Hence, we have reverted to the initial condition, namely 1 gr. mol. solution b of 100°, being 134,5 grams and during the circulation process we have converted 0,464 grm. mols of $NaNO_3$ or **0,345** grm. mols. per 100 grams of solution. On cooling, 0,6 mols. = 10,8 grams of water had to be added to this solution which on raising the temperature to 100° had again to be evaporated.

II. If we start again from a solution in which equivalent quantities of $NaNO_3$ and KCl are dissolved and allow the evaporation again to take place at 100°, but the crystallisation of KNO_3 at 25°, the final solution becomes c' (coinciding incidentally with P_2 at 25°) 0,64 NaCl, 0,36 KNO_3, 5,01 H_2O.

The reaction taking place when the liquid b is cooled, is then:

$$\frac{50}{59} \left\{\begin{array}{l} 0{,}59\ KNO_3 \\ 0{,}41\ NaCl \\ 2{,}83\ H_2O \end{array}\right\} + 0{,}321\ H_2O = 0{,}305\ KNO_3 + 0{,}504 \left\{\begin{array}{l} 0{,}64\ NaCl \\ 0{,}36\ KNO_3 \\ 5{,}01\ H_2O \end{array}\right\}.$$

The yield is now $100 \times \frac{0,305}{0,500} = 61\,\%$.

For the continuous process the transformations at 25° and 100° are expressed by the equations:

$$\underset{(b)}{\left\{\begin{matrix} 0,59\ KNO_3 \\ 0,41\ NaCl \\ 2,83\ H_2O \end{matrix}\right\}} + 0,379\ H_2O = 0,359\ KNO_3 + 0,641 \underset{(c')}{\left\{\begin{matrix} 0,36\ KNO_3 \\ 0,64\ NaCl \\ 5,01\ H_2O \end{matrix}\right\}}$$

and

$$0,641 \underset{(c')}{\left\{\begin{matrix} 0,36\ KNO \\ 0,64\ NaCl \\ 5,01\ H_2O \end{matrix}\right\}} + 0,359\ NaNO_3 + 0,359\ KCl = \underset{(b)}{\left\{\begin{matrix} 0,59\ KNO_3 \\ 0,41\ NaCl \\ 2,83\ H_2O \end{matrix}\right\}} + $$
$$+ 0,359\ NaCl + 0,379\ H_2O.$$

Per 1 grm. mol. of solution *b* only 0,359 grm. mol. of $NaNO_3$ has now been converted into KNO_3 or **0.267** grm. mol. per 100 grams of solution.

III. A solution in which KCl and $NaNO_2$ are present in equivalent quantities suffers from the defect that at the isothermic evaporation at 100° the saturation with KCl is already attained when only a comparatively small amount of NaCl has as yet deposited. The point *b* lies close to *a*.

If to the solution is added a small excess of $NaNO_3$ much more NaCl can deposit at 100°. The most favourable proportion is present in a solution which passes into the liquid P_2 (100°) with separation of NaCl. As the composition of P_2 is:

$$0,38\ Na, \quad 0,62\ K, \quad 0,20\ Cl, \quad 0,80\ NO_3, \quad 1,81\ H_2O$$

this solution must contain 0.80 grm.mol. of $NaNO_3$ and 0.62 grm.mol. of KCl. During the isothermic evaporation at 100° it deposits 0.42 mols. of solid NaCl.

If now the solid NaCl is again removed and the liquid P_2 cools to 5°, KNO_3 will crystallise out. The composition of the solution then changes in the direction KNO_3—P_2—*d*.

If no water is added, KNO_3 is deposited to such an extent that the solution *d* is attained, afterwards, along the line dP_1 (5°) also NaCl and finally in P_1 also $NaNO_3$. The transformation takes place according to the equation:

$$\underset{(P_2\ 100^\circ)}{\left\{\begin{matrix} 0,62 & K \\ 0,38 & Na \\ 0,80 & NO_3 \\ 0,20 & Cl \\ 1,81 & H_2O \end{matrix}\right\}} = 0,575\ KNO_3 + 0,038\ NaCl + 0,010\ NaNO_3 + 0,377 \underset{(P_1\ 5^\circ)}{\left\{\begin{matrix} 0,12\ K \\ 0,88\ Na \\ 0,57\ NO_3 \\ 0,43\ Cl \\ 4,80\ H_2O \end{matrix}\right\}}.$$

If, however, water is added, the separation of solid NaCl and $NaNO_3$ can be avoided and the solution *d* obtained as the final liquid which has the composition 0,13 K, 0,87 Na, 0,54 NO_3, 0,46 Cl, 4,99 H_2O. This separation takes place according to the equation

$$\underset{(P_2\ 100)}{\left\{\begin{array}{ll}0{,}62 & \mathrm{K}\\ 0{,}38 & \mathrm{Na}\\ 0{,}80 & \mathrm{NO_3}\\ 0{,}20 & \mathrm{Cl}\\ 1{,}81 & \mathrm{H_2O}\end{array}\right\}} + 0{,}371\ \mathrm{H_2O} = 0{,}563\ \mathrm{KNO_3} + 0{,}437\ \underset{(d)}{\left\{\begin{array}{l}0{,}13\ \mathrm{K}\\ 0{,}87\ \mathrm{Na}\\ 0{,}54\ \mathrm{NO_3}\\ 0{,}46\ \mathrm{Cl}\\ 4{,}99\ \mathrm{H_2O}\end{array}\right\}}.$$

As the solution P_2 can be obtained from 0,80 mol. $NaNO_3$ and 0,62 grm. mol. of KCl the yield, in this method of working, is of $NaNO_3$ $\frac{0{,}563}{0{,}800} \times 100 = \mathbf{70{,}4}\,\%$ and of KCl $\frac{0{,}563}{0{,}62} \times 100 = \mathbf{90{,}8}\,\%$.

In a continuous process the final solution *d* must be again converted into the solution P_2 (100°) which necessitates addition of fresh $NaNO_3$ and KCl (in equivalent proportions). On heating at 100° these salts pass into solution and NaCl is deposited. The entire decomposition takes place according to the equation:

$$0.437\ \underset{(d)}{\left\{\begin{array}{l}0{,}13\ \mathrm{K}\\ 0{,}87\ \mathrm{Na}\\ 0{,}54\ \mathrm{NO_3}\\ 0{,}46\ \mathrm{Cl}\\ 4{,}99\ \mathrm{H_2O}\end{array}\right\}} + 0{,}563\ \mathrm{KCl} + 0{,}563\ \mathrm{NaNO_3} = \underset{(P_2\ 100)}{\left\{\begin{array}{l}0{,}62\ \mathrm{K}\\ 0{,}38\ \mathrm{Na}\\ 0{,}80\ \mathrm{NO_3}\\ 0{,}20\ \mathrm{Cl}\\ 1{,}81\ \mathrm{H_2O}\end{array}\right\}} + 0{,}371\ \mathrm{H_2O} + 0{,}563\ \mathrm{NaCl}.$$

We now have once more the original liquid P_2, namely 1 grm.mol. or 122.2 gram, whereas during the circulation process 0,563 grm.mols. $NaNO_3$ have been transformed into KNO_3. Per 100 grams of the solution P_2 (100°) this is **0,461** grm.mols.

IV. If the lowest temperature we work at is not 5° but 25° the final solution becomes:

$$d' = 0.29\ \mathrm{K},\ 0.71\ \mathrm{Na},\ 0.627\ \mathrm{NO_3},\ 0.373\ \mathrm{Cl},\ 3.87\ \mathrm{H_2O}.$$

The transformation of P_2 (100°) into *d'* takes place as follows:

$$\underset{(P_2\ 100^\circ)}{\left\{\begin{array}{l}0{,}62\ \mathrm{K}\\ 0{,}38\ \mathrm{Na}\\ 0{,}80\ \mathrm{NO_3}\\ 0{,}20\ \mathrm{Cl}\\ 1{,}81\ \mathrm{H_2O}\end{array}\right\}} + 0{,}26\ \mathrm{H_2O} = 0{,}465\ \mathrm{KNO_3} + 0{,}535\ \underset{(d')}{\left\{\begin{array}{ll}0{,}29 & \mathrm{K}\\ 0{,}71 & \mathrm{Na}\\ 0{,}627 & \mathrm{NO_3}\\ 0{,}373 & \mathrm{Cl}\\ 3{,}87 & \mathrm{H_2O}\end{array}\right\}}.$$

Conversely the solution d' obtained will again have to take up 0,465 grm.mols. of KCl and $NaNO_3$ and deposit the same quantity of NaCl in order to pass into 1 gram.mol. P_2 (100). In this method of working 0,465 grm.mol. of salpetre are converted per grm.mol. P_2 100° (122,2 grams) that is **0,380** grm. mols. per 100 grams of solution.

If we compare the yields of these four processes, it appears that, in the continuous process, the transformation per 100 grams of solutions at 100° amounts to

0,345	grammolecules in the method of working	I
0,267	,, ,, ,, ,, ,, ,,	II
0,461	,, ,, ,, ,, ,, ,,	III
0,380	,, ,, ,, ,, ,, ,,	IV

Hence, III and IV give the largest transformation.

This is in agreement with the practical experience in the conversion. O. Dammer [1]) states about this, that, nowadays one does not add together KCl and $NaNO_3$ in exactly equivalent quantities but uses an excess of $NaNO_3$ so as to ensure a complete decomposition of the KCl.

We further notice that in all four processes, after heating at 100° and removing the NaCl, an addition of water is necessary to prevent simultaneous separation of NaCl with the KNO_3. In practice, this seems not to be done. The crude potash salpetre will, therefore, contain NaCl-crystals which are removed by washing with cold water.

Finally, I tender my sincere thanks to Miss J. Ph. van Rees and Mr. R. de Lange for their assistance and the care with which they have executed the analyses.

Laboratory for anorganic and physical chemistry
of the Technical High School.

Delft, January 1914.

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[1]) Handbuch der chemischen Technologie. I, 307 (1905).

Physics. — *"On the critical density for associating substances."* By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of March 28, 1914).

For non-associating substances the critical density is determined by the relation:

$$D_k = 0{,}001293 \frac{M}{28{,}84} \frac{p_k}{RT_k} s.$$

We then understand by density the number of grams that 1 cm^3 weighs, by M the molecular weight, and by s the factor introduced by SYDNEY YOUNG, which denotes how many times the critical volume is smaller than would be the case if the substance should have followed the laws of BOYLE and GAY-LUSSAC. So that s corresponds to the relation:

$$s \frac{p_k v_k}{RT_k} = \frac{p_0 v_0}{RT_0}$$

or as $p_0 = 1$ and $RT_0 = 1$, to:

$$s \frac{p_k v_k}{RT_k} = v_0 .$$

If we imagine a quantity of substance present equal to M, then $v_0 = \frac{28{,}84}{0{,}001293} = 22305$, and the given equation for D_k becomes duly:

$$D_k = \frac{M}{v_k} .$$

The determination of v_k is therefore sufficient for the determination of D_k, and also, when T_k and p_k are taken into account, for the determination of the quantity s. We owe it chiefly to SYDNEY YOUNG that the value of D_k and the corresponding value of s is known for a great number of substances. If the observations do not allow the direct determination of v_k, one may avail oneself of other methods to determine D_k for the calculation of s, but not with the same certainty, and determine the quantity s by the aid of this value and the knowledge of M, p_k, and T_k according to the above given formula. Now it is remarkable to how high a degree this quantity is found the same for alle non-associating substances, and how little it appears to differ from 3,77. Whether it really has this value for all normal substances, whether a smaller value will exist particularly for substances with small molecules, I will not discuss again at present, but I will point out that the appreciably larger values of s, which are given for associating substances by SYDNEY YOUNG, may be perfectly accounted for with this value of $s = 3{,}77$.

SYDNEY YOUNG (Proceedings Physical Society of Londen July 1894) gives $s = 5$ for acetic acid, $s = 4{,}52$ for methyl alcohol, $s = 4{,}02$ for ethyl alcohol, etc.

For associating substances a modification must be applied in the formula for D_k, which we have given above, namely in the value of M. Let there be present $1 - x_k$ single molecules, and x_k double molecules, then the molecular weight present in the critical state $= M_1(1 - x_k) + M_2 x_k$ and M_2 being $= 2M_1$, the molecular weight $= M_1(1 + x_k)$. Hence we get:

$$D_k = \frac{0{,}001293}{28{,}84} M_1 (1 + x_k) \frac{p_k}{RT_k} s$$

which, if

$$\frac{p_k v_k}{RT_k} s = v_0$$

is put again, agrees with:

$$D_k = \frac{M}{v_k} = \frac{M_1(1 + x_k)}{v_k}.$$

The ratio between the critical density and that which would be found when the laws of BOYLE GAY-LUSSAC were followed, is therefore greater for two reasons. First because of the existence of the quantity x_k, and secondly on account of the existence of $s > 1$. And SYDNEY YOUNG's value for acetic acid, viz. 5, is the product $s(1 + x_k)$. And assuming again 3.77 for s, we determine $1 + x_k = \frac{5}{3.77}$ or $1 + x_k = 1{,}324$. But we are only sure of this value of x_k, if we may assume $s = 3{,}77$ also in this case. And though this is probable, à priori, because the value of s, deviating from $\frac{8}{3}$, the value obtained when b is put invariable, only depends on the way in which b decreases, yet it seemed desirable to me to investigate this more closely. For this purpose I have examined the equation of state for an associating substance more accurately. It has the form:

$$p = \frac{RT}{v - b_k} - \frac{a_x}{v^2}.$$

The numerator, which would be equal to $R_1 T M_1 (1 - x) + R_2 T M_2 x$ may be written in this simple form, because $M_1 R_1 T = M_2 R_2 T$.

The value of b_x is $b_1(1-x)+b_2x$; or as $b_2=2b_1$, we find the value $b_1(1+x)$ for b_x. And the value of a_x consists of 3 terms, viz. 1. $a_1(1-x)^2$, the contribution yielded by the single molecules present. 2. $2\times 2a_1x(1-x)$, the attraction of the single molecules present exerted on the present double molecules and vice versa, and 3. the term. $(2a_1x)^2$. Joining these we find:

$$a_1(1-x+2x)^2=a_1(1+x)^2.$$

We can then reduce the equation of state to the following form:

$$p=\frac{\dfrac{RT}{1+x}}{\dfrac{v}{1+x}-b_1}-\frac{a_1}{\left(\dfrac{v}{1+x}\right)^2}.$$

When we compare this shape of the equation of state of the associating substance with that of the substance, when it would contain only single molecules, we see, that with given pressure and temperature $\dfrac{T}{1+x}=T_1$, a volume V_x of the associating substance corresponds to a volume V_1 of the single molecules, which volume V_x is $(1+x)$ times larger, and that over the entire region. Only the value of x is variable. And as I may suppose known, another equation, viz. $\left(\dfrac{d\psi}{dx}\right)_v=0$ is required for the determination of x. But at the moment we do not require the knowledge of the course of x.

A quantity M_1 of a substance, consisting only of single molecules, is in a volume v_1, and a quantity $M_1(1+x)$ of an associating substance is in a volume $v_1(1+x)$. The density is therefore the same for given p and $\dfrac{T}{1+x}$ in these cases. I had expected this result, and even pronounced it, though I may only consider this thesis as proved by the foregoing.

Before proceeding further in the investigation of the value of s for the associating substance, I will point out some particularities about the critical circumstances. We find for $(RT_k)_x$ by approximation:

$$(RT_k)_x=\frac{8}{27}\frac{a_1(1+x_k)^2}{(b_1)_k(1+x_k)}=\frac{8}{27}\frac{a_1}{(b_1)_k}(1+x_k),$$

and for $(p_k)_x$:

$$(p_k)_x=\frac{1}{27}\frac{a_1(1+x_k)^2}{(b_1)_k(1+x_k)^2}=\frac{1}{27}\frac{a_1}{(b_1)_k^2},$$

and for $\dfrac{(RT_k)_x}{(p_k)_x}$ the value $8(b_1)_k(1+x_k)$, and as $(b_1)_k$ is smaller than $(b_1)_g$, about:

$$\frac{(RT_k)_x}{(pk)_x} = 7\,(b_1)_g\,(1+x_k) = \frac{RT_{k_1}}{pk_1}\,(1+x_k).$$

For the quantity $\frac{T_k}{pk}$ we find (see my preceding communication p. 889, These Proc. Feb. 1914) the value of 10,415 much too large for $\frac{T_{k_1}}{pk_1}$. Also by comparison of these values $(1+x_k)$ might be determined, but with less certainty.

The critical temperature of an associating substance is therefore greater than might be inferred from the molecular size of the single molecule — but the critical pressure has not changed.

Let us now return to the determination of $\frac{pv}{T}$ for the critical circumstances of the associating substance, and compare this with $\frac{pv}{T}$ for the critical circumstances for permanent single molecules. For the associating substance this value is equal to $\left(\frac{pkvk}{Tk}\right)_x$. If we replace the value of (v_k) by $(1+x)\,v_1$ for $(pk)_x$ and $(T_k)_x$, we have to determine the value of $\frac{(T_k)_x}{(pk)_x}\,v_1\,(1+x_)$, and if we now substitute (pk_1) for $(pk)_x$, and (Tk_1) $(1+x)$ for $(T_k)_x$, the required value becomes equal to:

$$\frac{(pk)_1\,v_1}{(T_k)_1}.$$

And now we have still to show that $v_1 = (v_k)_1$.

If b is variable, the critical volume is, indeed, not $3b_g$, but $l\,b_g$, in which l is somewhat smaller than 2, or $l'\,bk$, when l' is somewhat greater than 2, so that $(v_k)_x = l\,b_g\,(1+x_k)$. On the supposition that l has the same value for all substances, at least for substances with not too small a number of atoms in the molecule, we have shown by this that

$$\left(\frac{pkvk}{Tk}\right)_x = \left(\frac{pkv_rk}{Tk}\right)_1$$

and that therefore the quantity s may be put equal to 3,77 also for the associating substance.

The foregoing considerations are not confined to cases in which real association exists, but may also be applied to cases in which what I have called quasi association is found. This probably occurs already to an appreciable degree in the critical circumstances for alcohols. In case of real association there are double and triple molecules present, the possibility of the existence of which chemistry must be able to show by means of the construction of the molecule; in case of quasi-association, however, there are local accumulations of molecules, which may lead to the question if the cause why they occur in a greater degree for one substance than for another, may perhaps be found in the form of the molecules. But this question cannot be answered with any certainty yet. Nor can the question be answered as yet for real association why for acetic acid and for aldehydes and perhaps some other substances as nitriles, this association exists

The degree of aggregation for the quasi-association will probably not be the same for each of these aggregations, but to simplify the calculation we may assume on an average the value n for it, which I estimated already before at 8 or 9. It is, however, to be expected that also the mean value n will vary with pressure and temperature. But since we have only to examine the influence of the quasi association on the critical circumstances here, we may confine ourselves to an invariable value of n. Proceeding here as we did above, we find for $1-x$ non aggregated molecules, and x aggregations the molecular weight equal to $M_1(1-x+nx)$. For b_k we find $b_1(1-x+nx)$ and for a_k the value $a_1\{1-x+nx\}_2$.

And we may write the equation of state:

$$p=\frac{\dfrac{RT}{1+(n-1)x}}{\dfrac{v}{1+(n-1)x}-b_1}-\frac{a_1}{\left[\dfrac{v}{1+(n-1)x}\right]^2}.$$

Hence with given pressure and temperature $\dfrac{T}{1+(n-1)x}=T_1$ is $\dfrac{v_k}{1+(n-1)x}=v_1$, if we should call v_1 the volume which the substance would occupy at the same pressure and corresponding temperature, when it were not in quasi-association. The value of $v=v_1(1+(n-1)x)$. In the first case the density is equal to $\dfrac{M_1}{v_1}$ in the second to $\dfrac{M_1(1+(n-1)x)}{v}$, so of the same value. Thus we shall also find:

$$D_k=\frac{0{,}001293}{28.84}M_1[1+(n-1)x_k]\frac{(p_k)_x}{(RT_k)_x}$$

$$(T_k)_x=(T_k)_1[1+(n-1)x_k]$$

$$(p_k)_x=(p_k)_1$$

and

$$(V_k)_x=(v_k)_1[1+(n-1)x_k]$$

And so also:

$$\left(\frac{p_kv_k}{T_k}\right)_x=\left(\frac{p_kv_k}{T_k}\right)_1$$

According to the values given by SYDNEY YOUNG $s[1+(n-1)x_k$ has the value 4,52 for methyl alcohol, 4,02 for ethyl alcohol, and also 4,02 for propyl alcohol. With $s=3.77$ we found for:

Methyl alcohol $1+(n-1)x_k=1{,}2$
Ethyl alcohol $1+(n-1)x_k=1{,}0663$
Propyl alcohol $1+(n-1)x_k=1.0663$

Now for these three substances $\left(\frac{T_k}{p_k}\right)_x$ is respectively equal to:

6,52, 8,2 and 10,7.

By the aid of the value of $1+(n-1)x_k$ for these three substances we calculate $\left(\frac{T_k}{p_k}\right)$ or b_1, and then we find:

5,43, 7,69 and 10,03

The differences are almost equal, viz. 2.26 and 2.34, but they are smaller than what we have found for CH_2 in the series of the saturated hydrocarbons, and this seems inexplicable for the time being. Unless we might assume that an atom C, when bound to O, is smaller than when it is bound to H, and that besides it could also impart this property to other atoms C to which it is bound. The value for ethyl alcohol calculated here is, however, in perfect agreement with the value for ether calculated in the preceding communication. With b for ether equal to 13,12 follows the value 7.60 for alcohol by subtraction of 2×2.76. For methyl ether, for which we found $b=7.55$ before, we could now find 5.43, by putting $CH_2=2.12$. But this is possible, when C bound to O should be smaller than C bound to C. The difference, however, is then greater than could be expected. So that we are again confronted with the question whether in case of quasi-association circumstances occur which we have not yet duly taken into account in our discussion. This, however, is quite beside the subject of this communication which purposes to show that we may consider the quantity s as entirely, or almost entirely of the same value at least for polyatomic molecules. The slight differences are then entirely subject to the relation given by me before $\frac{s^2}{f-1}=\frac{64}{27}$, which, however, only holds unmodified for normal substances; the value of s for associating substances has been discussed here, and a closer investigation about the value of f for such substances would also be desirable.

Physics. — *"On the law of partition of energy."* V. By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of March 28, 1914).

§ 10 bis. In § 10 of this series of communications[1]) I have drawn up a formula for the dissociation equilibrium of a di-atomic gas. This formula, however, requires emendation. In the first place, namely, the c_v of the gas would not correspond with 5, but with 7 degrees of freedom on the suppositions introduced l. c. And besides the vibrations of the atom would consist of three equivalent degrees of freedom, and there was no occasion to ascribe the ordinary equipartition amount to two of them (together representing a rotation round the other atom), and the amount U of PLANCK's formula to the third (the vibration in the direction of the radius vector).

To correct this we shall have to take care that the degrees of freedom do not remain equivalent. Then it will no longer be permissible to consider one atom as a point which moves in the quasi elastic region of the other. We shall then introduce the following suppositions. Every atom will have a point P, which we shall call the pole. The line from the centre M to the pole will be called *axis*. There will be a quasi elastic region G round the pole. Two atoms will now be bound when they lie with their poles in each other's regions G. The potential energy will be minimum when the poles coincide, and when moreover the axes are one another's continuation.

We shall introduce the following coordinates for the diatomic molecules:

1. The three coordinates of the centre of gravity x_z, y_z, z_z. The kinetic energy corresponding to them will be $\frac{3}{2}\theta$.

2. The distance of the centres of the atoms, or rather the displacement in the direction $M_1 M_2$ of the points P_1 and P_2 out of the state of equilibrium (in which they coincided). This displacement will be called r; it will give rise to vibrations with the frequency ν, in which the potential and the kinetic energy are both equal to $\frac{1}{2}U$.

3. Displacements of P_1 and P_2 with respect to each other normal to $M_1 M_2$, or what comes to the same thing rotations of the axes out of the position $M_1 M_2$. These coordinates will give rise to rotative

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[1]) These Proc. XVI, p. 88.

vibrations. In agreement with RUTHERFORD, PERRIN, and others I shall assume the moment of inertia of the atom to be very small, even in comparison with ma^2 ($m =$ mass, $a =$ radius of the atom). Then the frequency of this rotative vibration will be great compared with ν. In connection with this we shall put the energy of these vibrations equal to zero, and entirely disregard possible atomic rotations.

4. The rotation of the molecule. Of this we may assume for all the cases of equilibrium that have been experimentally investigated that they represent two degrees of freedom, which present the equipartition amount, whereas the rotation round $M_1 M_2$ practically has an energy zero. We shall represent the position of the axis of the molecule by the aid of the angles α and β indicating the longitude and the latitude.

Instead of equation (19) p. 88 loc. cit. we now find for the number of dissociated pairs of atoms:

$$\left.\begin{aligned} n_1 &= N^2 e^{-\frac{\varepsilon_0}{\theta}} \int e^{-\frac{\varepsilon_0}{\theta}} dx_1 dy_1 dz_1 \left(m_1\right)^3 d\dot{x}_1 d\dot{y}_1 d\dot{z}_1 \times \\ &\times dx_2 dy_2 dz_2 \left(m_2\right)^3 d\dot{x}_2 d\dot{y}_2 d\dot{z}_2 = \\ &= N^2 e^{-\frac{\varepsilon_0}{\theta}} \left(2\pi m_1 \theta\right)^{3/2} \times \left(2\pi m_2 \theta\right)^{3/2} \end{aligned}\right\} \quad . \quad . \quad (19a)$$

For the number of bound pairs of atoms we find, representing the moment of inertia of the molecule by M:

$$\left.\begin{aligned} n_v &= N^2 e^{-\frac{\varepsilon_1}{\theta}} \int e^{-\frac{\varepsilon_p + {}^1/_2 fr^2}{\theta}} \chi(r\dot{r}v) dx_z dy_z dz_z (m_1+m_2)^3 d\dot{x}_z d\dot{y}_z d\dot{z}_z \times \\ &\times dr \frac{m_1 m_2}{m_1+m_2} d\dot{r} \sin^2 \alpha d\alpha d\beta M^2 d\dot{\alpha} d\dot{\beta}. = \\ &= N^2 e^{-\frac{\varepsilon_1}{\theta}} \{2\pi (m_1+m_2) \theta\}^{3/2} \frac{h}{1-e^{-\frac{vh}{\theta}}} \times 4\pi \times 2\pi M\theta \end{aligned}\right\} \quad (19'a)$$

For ε_p depends on $\dot{r}$ through the term $\frac{1}{2} \frac{m_1 m_2}{m_1+m_2} \dot{r}^2$, which term we shall call ε_{pr}. In connection with this equation (18) loc.cit. must now be written as follows:

$$\int e^{-\frac{\varepsilon_{pr} - {}^1/_2 f r^2}{\theta}} \chi (r \dot{r} v) \frac{m_1 m_2}{m_1 + m_2} d\dot{r}\, dr = \frac{h}{1 - e^{-\frac{vh}{\theta}}}$$

This gives for the equilibrium constant:

$$\frac{n_1{}^2}{n_{\nu}} = e^{\frac{\varepsilon_1 - \varepsilon_0}{\theta}} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{3/_2} \frac{1}{M} \times \frac{1 - e^{-\frac{vh}{\theta}}}{h} \times \frac{1}{2} \sqrt{\frac{\theta}{2\pi}} \,. \quad (20a)$$

§ **13**. *Zero point energy and chemical binding.*

In the above given formula PLANCK's later supposition concerning the existence of a zero point energy has not been taken into account. We shall now examine some consequences of this supposition for the chemical phenomena. In the first place we shall show that according to this supposition the entropy of a number of particles does not change at the absolute zero point, when they pass from a binding in which they can vibrate with a definite period into another combined state, in which they have another period. For this purpose we shall make use of BOLTZMANN's quantity H, which we shall represent as follows:

$$H = \int F\, l \left(F \right) m^3 d\dot{x} d\dot{y} d\dot{z}\; dx dy dz.$$

So we think here again of a three dimensional vibrator with three equivalent degrees of freedom, though this case probably never occurs in reality. If we had taken a linear vibrator, this would have come to the same thing. But then we should have had to speak besides of vibrations, also of rotations of the molecule, which would have rendered the question somewhat less simple.

According to PLANCK's supposition the value of F for $T = 0$ is constant for an energy smaller than $v\, h$, equal to zero for a larger energy. Let us put:

$$m^3\, dx dy dz\; d\dot{x} d\dot{y} d\dot{z} = d\omega,$$

and

$$\int\limits_{\varepsilon < \nu h} m^3\, d\dot{x} d\dot{y} d\dot{z}\; dx dy dz = G$$

then for $T = 0$:

$$\int F d\omega = F \int d\omega = FG = N,$$

when N represents the total number of particles, and further:

$$H = l(F) \,.\, \int F d\omega = l(F) \,.\, N = N \{ l(N) - l(G) \}.$$

We may write for G:

$$G = \frac{m^{3/2}}{f^{3/2}} \int\limits_{\varepsilon < \nu h} dx_1\, dx_2\, dx_3\, dx_4\, dx_5\, dx_6$$

when we introduce $\dot{x}\sqrt{m} = x_1$, $\dot{y}\sqrt{m} = x_2$, $\dot{z}\sqrt{m} = x_3$, $x\sqrt{f} = x_4$, $y\sqrt{f} = x_5$ and $z\sqrt{f} = x_6$, so that $\varepsilon = x_1^2 + x_2^2 + x_3^2 + x_4^2 + x_5^2 + x_6^2$.

The integral occurring in G, therefore, represents the content of a sixdimensional sphere with a radius $\sqrt{\nu h}$, and is therefore proportional to $(\nu h)^3$. Bearing in mind that $\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}}$, we see that G and with it also H, becomes an absolute constant.

If we assume for a linear vibrator that besides vibrations with a frequency ν rotations occur with a frequency $\nu' = \frac{h}{2\pi^2 M}$, it appears here in the same way that G and H become absolute constants.

Hence we see that on these simple suppositions Planck's supposition about the zero point energy directly leads to Nernst's heat theorem.

As known Planck formulated Nernst's theorem by assuming that the entropy remains finite at $T = 0$, and does not become $-\infty$, as it would have to do according to the older theory. According to the older theory, e. g. according to Boltzmann, one would *have to* come to the value $-\infty$, because at $T = 0$ the molecules would all have a velocity zero, and there would, therefore, be only one possible distribution of the points of velocity in the diagram of velocity. At every higher temperature there would be ∞ many velocities possible for every molecule; there would therefore be infinitely many possible distributions of the points of velocity. The probability at higher temperature would therefore be ∞ times as great as at $T = 0$, which leads to an ∞ difference of entropy.

It is interesting to observe how the two suppositions introduced by Planck into physics evade this difficulty and make the entropy difference finite in the two only ways possible. The infinite entropy difference could namely be evidently evaded in two ways; namely 1. by assuming that there is a finite number of distributions of the points of velocity also at high temperature, and 2. by assuming that there are infinitely many also at $T = 0$. The former hypothesis is that of the energy quanta, the second that of the zero point energy. Each of these two suppositions leads to a finite relation of the number of possible distributions at $T = 0$ and at $T > 0$, and hence to a finite entropy difference.

Let us now examine the distribution of the energy at higher temperature. We shall continue to assume that a number of molecules will possess an energy $< \nu h$, and that for them every value of the energy is equally probable. So in this region the chance that the energy lies between ε and $\varepsilon + d\varepsilon$ will be represented by $F(\theta\nu)\, d\varepsilon$. In the region where $\varepsilon > \nu h$ I shall continue to assume that the function is represented by $e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon\nu)\, d\varepsilon$ [1]. If we now put:

$$I = \int_0^{\nu h} F(\theta\nu)\, d\varepsilon + \int_{\nu h}^{\infty} e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon\nu)\, d\varepsilon \quad . \quad . \quad . \quad . \quad . \quad (21)$$

the equilibrium constant of a chemical conversion is represented by:

$$K = e^{-\frac{\Delta\varepsilon}{\theta}} \Pi I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20b)$$

In this $\Delta\varepsilon$ represents the difference in potential energy which would occur when the substances passed from the compounds of the lefthand member of the reaction equation into those of the righthand member. In order to obtain the energy amount $\Delta\varepsilon$ then, it would however be necessary that the atoms in the compounds always occupied the positions of minimum potential energy, so in the centres of the quasi elastic regions. ΠI represents a fraction with the product of the quantities I, referring to substances in the lefthand member in the numerator, and with that in the righthand member in the denominator. The equation is evidently nothing but a generalisation of (20a), in which besides the I's are determined in agreement with the supposition of the zero point energy.

Now

$$\frac{dlK}{d\theta} = + \frac{\Delta\varepsilon}{\theta^2} + \Sigma \frac{1}{I} \frac{dI}{d\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

On the other hand the law of the equilibrium change requires:

$$\frac{dlK}{d\theta} = \frac{Q}{\theta^2} = \frac{Q_0 + \Sigma \int_0^T C_v dT}{\theta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22a)$$

Further we have:

$$Q_0 = (\Delta\varepsilon + \Sigma \tfrac{1}{2} \nu h) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

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[1] Besides in my previous communications this function had already been introduced by EHRENFEST, Ann. d. Phys. IV, **36** p. 91, Ann. 1911, which paper I have not sufficiently taken into account in my previous considerations; the same refers to POINCARÉ's paper, Journal de Physique theor. et appl. V serie II p. 5. Ann. 1912.

$$\Sigma \frac{\theta^2}{I} \frac{dI}{d\theta} = \Sigma \tfrac{1}{2} v h + \Sigma \int_0^T C_v dT = \Sigma\, U \quad . \quad . \quad . \quad . \quad (23a)$$

In all these summations the quantities must have the sign $+$ or $-$ according as they relate to the righthand or the lefthand member of the reaction equation. The equations having to hold for every chemical reaction, independent of the values of the v's, we shall be allowed to omit the Σ signs in (23a), and write such an equation for every coordinate separately.

We then get:

$$U = \frac{\int\limits_0^{\nu h} \varepsilon\, F(\theta,v)\, d\varepsilon + \int\limits_{\nu h}^{\infty} \varepsilon e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon,v) d\varepsilon}{I} = \frac{\theta^2}{I} \frac{dI}{d\theta}$$

or

$$\frac{1}{2} (vh)^2\, F(\theta,v) + \int\limits_{\nu h}^{\infty} \varepsilon e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon,v) d\varepsilon = \theta^2 \left\{ \int\limits_0^{\nu h} \frac{dF}{d\theta} d\varepsilon + \int\limits_{\nu h}^{\infty} \frac{\varepsilon}{\theta^2} e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon,v)\, d\varepsilon \right\}$$

or

$$\frac{1}{2} (vh)^2\, F(\theta,v) = \frac{dF(\theta,v)}{d\theta}\, \theta^2 \,.\, vh \,.$$

from which follows:

$$F(\theta v) = C \times e^{-\frac{vh}{2\theta}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

It is evidently not impossible to assign such a value to the C that $F(\theta,v)$ and $e^{-\frac{e}{\theta}} \chi(\varepsilon,v)$ continuously pass into each other at more than a single temperature. In general a discontinuity will occur in the function of probability at $\varepsilon = vh$. I do not know a way to determine C. The value $\chi(\varepsilon,v)_{\varepsilon = vh}$ suggests itself most naturally. Then the function of probability becomes continuous at $\theta = \infty$, which is in accordance with the fact that at high temperatures the deviations from classical mechanics become smaller. With this value of C we see that the number of molecules having an energy slightly smaller than vh, is greater that the number having a somewhat greater energy. The ratio is $e^{\frac{hv}{2\theta}}$. This is in harmony with PLANCK's theory according to which for vibrators which are absorbing energy of radiation, only a part continues to absorb when $\varepsilon = vh$

is reached, and passes therefore to the group for which $\varepsilon > vh$, whereas another part emits all the stored energy. For the chance of emission we find another value than PLANCK. This is not astonishing as we assumed that for $\varepsilon > vh$ the function of probability would be continuous, whereas according to PLANCK it exhibits new discontinuities at $\varepsilon = 2vh$ etc. At all events we see that PLANCK's hypothesis concerning the zero-point energy can only be reconciled with the thermodynomic law of the equilibrium change, when the function of probability shows a discontinuity at $\varepsilon = vh$, of entirely the same nature as had already been assumed by PLANCK.

In conclusion we will calculate I, as this quantity occurs in the formula for the equilibrium constant. Integration of (23a) with $U = \frac{vh}{e^{\frac{vh}{\theta}} - 1} + \frac{1}{2} vh$ yields:

$$I = \frac{h e^{-\frac{1}{2}\frac{vh}{\theta}}}{1 - e^{-\frac{vh}{\theta}}}$$

This expression differs from the value which we found without zero-point energy, and which we shall call I' by the factor $e^{-\frac{1}{2}\frac{vh}{\theta}}$. Hence we may write (20$b$) in the following form:

$$K = e^{-\frac{\Delta\varepsilon}{\theta}} e^{-\frac{1}{2}\Sigma\frac{vh}{\theta}} \Pi I'.$$

And Q_0 being $= (\Delta\varepsilon + \Sigma \frac{1}{2} vh)$, we find the same expression as without zero point energy, since then $Q_0 = \Delta\varepsilon$, and we may, therefore, always write:

$$K = e^{-\frac{Q_0}{\theta}} \Pi I'.$$

Chemistry. — "*A new hydrocarbon from the pinacone of methylethylketone*". By Prof. P. VAN ROMBURGH and Miss D. W. WENSINK.

(Communicated in the meeting of March 28, 1914).

When studying the action of formic acid on this pinacone this seemed to take a course quite contrary to expectation. Whereas in this reaction the ordinary pinacone is almost completely converted into pinacolin, a considerable quantity of a hydrocarbon is obtained here in addition to a pinacolin. A formate of the pinacone could not be isolated.

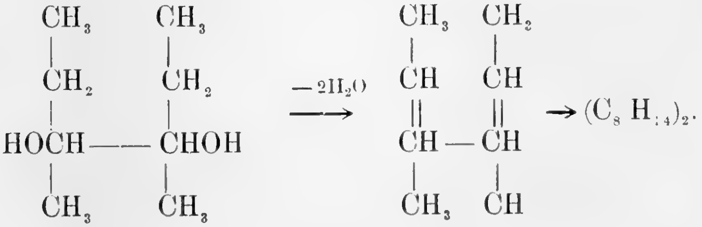
If we treat pinacone from methylethylketone with an equal weight of 97 °/$_0$ formic acid, the liquid, particularly on warming, turns a beautiful red colour and after about a quarter of an hour's heating in a waterbath, the homogeneous mixture separates into two layers, the upper one of which is nearly colourless. The bottom layer which has a dark red colour gives, when diluted with water, a pale coloured supernatant layer. The united layers were washed with water and dried over potassium carbonate. On distilling at the ordinary pressure up to 150° a liquid was obtained which proved to consist mainly of the pinacolin $(CH_3)_2 . C_2H_5 . C . CO . C_2H_5$.

The residue was distilled in vacuo when as main product was obtained a pale yellow viscous liquid b. p. 130°. By fractionating over metallic sodium a colourless distillate with an agreeable odour was finally obtained. $d^{13.5}_{4} = 0.8741$; $n^{13.5}_{D} = 1.4864$. $MR_D = 72.3$ calculated for $C_{16} H_{28} \overline{|=}_2$ 72.9.

The elementary analysis gave: C 86.96, 87.16; H 13.17, 12.82°/$_0$. Calculated for $C_{16} H_{28}$: C 87.27, H 12.72 °/$_0$.

The determination of the molecular weight (by means of the lowering of the freezing point of benzene) gave 216.3 and 207; calculated for $C_{16} H_{28}$ 220.

HERSCHMANN [1]) found that by the action of concentrated sulphuric acid at 0° pinacolin occurs only, but on heating with 5 °/$_0$ sulphuric acid was formed, besides pinacolin, also a hydrocarbon $C_8 H_{14}$ b. p. 117°—121°, which, as noticed by us, is converted on heating with formic acid into a dimeride identical with our hydrocarbon $C_{16} H_{28}$.



$$\begin{array}{ccc} \begin{array}{cc} CH_3 & CH_3 \\ | & | \\ CH_2 & CH_2 \\ | & | \\ HOCH & \!\!-\!\!-\!\!-\; CHOH \\ | & | \\ CH_3 & CH_3 \end{array} & \xrightarrow[\hspace{1cm}]{-2H_2O} & \begin{array}{cc} CH_3 & CH_2 \\ | & | \\ CH & CH \\ \| & \| \\ CH & \!\!-\; CH \\ | & | \\ CH_3 & CH \end{array} \end{array} \rightarrow (C_8 H_{14})_2.$$

One might imagine the structure of the hydrocarbon $C_{16} H_{28}$ to be like that of an octomethylcyclo-octadiene:

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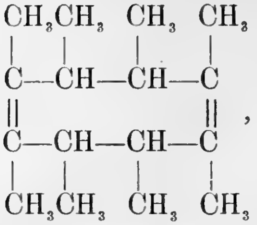
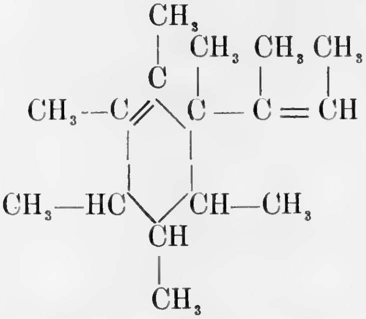
[1]) Monatshefte **14**, 233 (1893).



or in connexion with the researches of LEBEDEV [1]) on polymeric hydrocarbons, like:



In order to elucidate the structure we have already made a great many experiments which, however, have not yet led to definite results.

If the hydrocarbon is treated with bromine there always takes place, besides the addition, an evolution of hydrogen bromide even in very strong dilution and cooling to —40°, and we did not succeed in isolating a well-defined compound. An effort was made to reduce the dimeride with sodium and alcohol, but it did not take up any hydrogen under those conditions. Reduction with hydrogen under the influence of platinum or palladium was also applied by us in vain, up to the present.

Oxidation with potassium permanganate has also failed to lead to positive conclusions. Experiments intended to attain the desired result with ozone are in progress.

Utrècht. *Org. Chem. Lab. University.*

Chemistry. — "1 : 3 : 5 *Hexatriene*." By Prof. P. VAN ROMBURGH and Dr. P. MULLER.

(Communicated in the meeting of March 28, 1914).

One of us (v. R.) prepared in 1905, with Mr. VAN DORSSEN, the above hydrocarbon by heating the formate of s-divinylglycol.

From this could be obtained by addition of bromine:

1. a dibromide $C_6H_8Br_2$ that proved identical with the s-divinylethylene bromide prepared by GRINER. [2])

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[1]) Journ. Chem. Soc. **104** Abstr. 1285, (1913).

[2]) Ann. d. Chimie et de phys. (6) **26**, 367 (1892).

2. a tetrabromide $C_6H_8Br_4$ also already described by GRINER of the formula $CH_2{=}CH\text{-}CHBr\text{-}CHBr\text{-}CHBr\text{-}CH_2Br$.

3. a hexabromide $C_6H_8Br_6$ having the formula of a 1 : 2 : 3 : 4 : 5 : 6 hexabromohexane.

Addition of 6 atoms of hydrogen by the SABATIER and SENDERENS method gave normal hexane.

Although it was thus shown with certainty that by the process employed the desired unsaturated hydrocarbon was obtained, there remained some doubt as to its absolute purity, for instance, because the physical constants of the different preparations did not quite agree. It was, therefore, desirable to make efforts to get at a method that could yield this compound, sc important from a theoretical point of view, in a perfectly pure condition. After many tedious experiments we have at last succeeded.

First of all we tried to gain our object by modifications in the old method; after many experiments the following *modus operandi* was found to give the best results.

s-divinylglycol is heated with an equal weight of 99°/₀ formic acid for half an hour at 105°, the excess of acid is then distilled off in vacuo at 60° and the mixture of formates is decomposed rapidly by heating at the ordinary pressure at 160°—220°. The upper layer of the distillate is washed with water and distilled in an atmosphere of carbon dioxide or hydrogen, so as to avoid oxidation, up to 110° and the liquid obtained is dried over fused calcium chloride. Owing to the modifications introduced the yield of hydrocarbon is considerably larger and amounts to 40°/₀ of the glycol used.

A careful fractionate distillation of the hydrocarbon obtained did not, however, give even now a product with a constant boiling and melting point.

Experiments made to purify the preparation by freezing, although rising the initial fusion range[1]) could not be continued as the quantity at disposal was not sufficient. Hence, another method of preparing had to be looked for.

It was to be expected that by the action of dehydrating agents on hexadiene 1.5-ol 1.4 the desired hydrocarbon might form. This alcohol, obtained by Mr. LE HEUX[2]) according to FOURNIER's method, was treated with potassium pyrosulphate or phthalic anhydride. From 80 grams of the alcohol could be obtained by heating with 5—10 grams of potassium pyrosulphate 24 grams, and by heating

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[1]) The initial fusion traject was —55° to —47°.5, the final —47°.5 to —33°.

[2]) This Proceedings, Febr. 1913, p. 1184.

with the theoretical quantity of phthalic anhydride 30 grams of a product boiling below 100°, which, however, on continued purification, yielded the same amount of hexatriene. The boiling point ($80°.3$—$82°$) as well as the melting point (—$34°.5$ to —$29°$) was higher than that of the hydrocarbon prepared by the first method; a pure product could, however, not be obtained from the quantity at disposal.

Hence, we had recourse to the preparation from a crystallized substance namely from the above mentioned dibromide $C_6H_8Br_2$ prepared, according to GRINER, by the action of phosphorus tribromide on s.-divinylglycol. The bromide purified by recrystallisation gives, on treating the boiling alcoholic solution with zinc dust, a good yield of pure hexatriene. This was placed over fused calcium chloride so as to remove water and alcohol. After fractionating in an atmosphere of carbon dioxide or hydrogen a liquid was obtained (b.p. $80°.5$—$82°$ at 765 m.m.) which solidified in a mixture of ice and salt and melted at —$11°.5$ to —$9°.5$. $d_4^{16.7} = 0.7355$. $n\,d_D^{16.7} = 1.5150$.

$$MR_D = 32.82. \text{ Calculated for } C_6H_8|\overline{3} = 28.5.$$

For the specific exaltations were found:

$$E\Sigma_\alpha = 5.11$$

$$E\Sigma_D = 5.39$$

$$E\Sigma_\beta - E\Sigma_\alpha = 1.26 = 136.5\,{}^0/_0$$

$$E\Sigma_\gamma - E\Sigma_\alpha = 2.23 = 152\,{}^0/_0$$

As will be noticed, the specific exaltations of the refraction reach a remarkably high figure.

If we allow bromine to act on a solution of the pure hexatriene in carbon tetrachloride or carbon disulphide, s-divinylethylenebromide, m.p. 87°, is obtained quantitatively.

Hexatriene gets readily polymerised, particularly on warming. As in the above mentioned preparation of the hydrocarbon a fractional distillation at the ordinary pressure was applied for the purpose of purification, there was a chance that in this operation the distillate also might be contaminated with the polymeride.

Therefore, a new supply was prepared which was dried, first over calcium chloride and then over potassium hydroxide[1]; it then exhibited the following constants: m.p. $=$—$11°$; b.p. $= 80°$—$80°.5$ (at 755 mm.) $d_4^{12.5} = 0.7432$. $n_D^{12.5} = 1.5183$; $MR_D = 32.6$.

After a distillation in vacuo at which the hydrocarbon passed over

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[1] If the hydrocarbon is pure, the KOH remains uncoloured. If, however, it contains oxidation products, the latter turns brown at the surface.

at the temperature of the room and was cooled in a mixture of solid carbon dioxide and alcohol it gave the following results: m.p. $= -10°.5$; $d^{13.5}_4 = 0.740$; $n^{13.5}_D = 1.5172$; $MR_D = 32.7$.

After standing for a week over potassium hydroxide this liquid was again distilled at the ordinary pressure. Now was found: m.p. $-11°$ to $-10°$; $d^{14}_4 = 0.7396$; $n^{14}_D = 1.5167$; $MR_D = 32.7$.

From this we notice that the distillation at the ordinary pressure exerts no influence on the properties of the hydrocarbon so that the above-cited constants may be really taken to be those of pure hexatriene. The results mentioned here briefly, will be communicated more fully elsewhere.

Utrecht. *Org. Chem. Lab. University.*

Chemistry. — *"On dichloroacetylene"*. (A warning). By Prof. J. Böeseken and J. F. Carrière. (Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of March 28, 1914).

Our object was to prepare di-trichlorovinylketone from thrichloro-acrylic acid by elimination of carbon dioxide and water.

It was, therefore, first attempted to effect this decomposition by a careful dry distillation of the barium salt:

$$(CCl_2:CCl.COO)_2\,Ba = Ba\,CO_3 + (CCl_2:CCl)_2\,CO.$$

In a provisional investigation it appeared however, that a strong charring took place, whilst the barium was left in the form of chloride.

When the experiment was repeated much carbon dioxide was evolved and further a gas with a disgustingly sweet odour, which formed a strong nebula in contact with the air.

This nebula formation was coupled with a decided chemo-luminiferous phenomenon, so that we suspected that the most simple carbon chloride *dichloroacetylene* had formed according to the equation.

$$(CCl_2:CCl.COO)_2\ Ba = BaCl_2 + 2\,CO_2 + 2\,C_2Cl_2$$

As we had to take into account the possibility of dealing with a very explosive compound, a quantity of only one gram of the barium salt was slowly heated in a dry current of hydrogen. After first passing the gases through an empty suction tube, in which a fairly large quantity of bye-product (with high b.p.) was retained, they passed through a similar tube placed in a Dewar vessel in which the temperature was brought to $-70°$.

In this remained a little of a colourless, solid substance which melted below $-50°$ to a mobile, colourless drop of liquid.

In order to prove that this contained C_2Cl_2 chlorine was passed without opening the apparatus; after this had been able to act for some time at — 50°, the tube was brought to the ordinary temperature; C_2Cl_6 was left behind, which by its odour and sublimation phenomena was identified with the pure substance from the collection.

If the gas diluted with hydrogen was allowed to pass through a layer of water into the air, the same phenomena were noticed as with liquid hydrogen phosphide; each bubble coming into contact with the air forms a nebulous ring.

In a second experiment we started with three grams of barium trichloroacrylate; in the decomposition a more considerable secondary reaction took place so that, finally, the quantity of C_2Cl_2 collected was estimated not to exceed half a gram.

When, however, the apparatus was removed, this quantity exploded with the fatal result that one of us (CARRIÈRE) suffered a very serious injury to the eye.

Hence, dichloroacetylene is decidedly much more dangerous than dibromoacetylene [1]), because it decomposes with explosion by slight mechanical influences even without exposure to the air.

We have discontinued our researches in this direction and think we must warn our colleagues against this exceedingly treacherous compound.

The decomposition of barium trichloroacrylate is in agreement with that of the β-halogenates in general where the elimination of the metallic haloid salt must be considered as the first phase of the reaction.

It is remarkable that also in the case of chlorine atoms combined with unsaturated carbon, this tendency to form salts is so great that an energetic compound such as dichloroacetylene can be formed in considerable quantities.

Let us summarize the properties of dichloroacetylene:

It is a colourless gas with a disgustingly sweet odour. [2]) In a very diluted condition it exhibits chemo-luminosity; in a somewhat more concentrated form in admixture with H_2 and a little CO_2 it takes fire in the air.

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[1]) LEMOULT C. R. **136**, 55 (1903); **137**, 1333 (1903).

[2]) It is probable that Dr. PRINS has already observed this substance in the decomposition of one of the higher condensation products of $CH\,Cl^3$ with $C^2\,Cl^3\,H$; there was then also formed from a *hydrogen-free* carbon chloride compound under the influence of an alkali, a gas exploding in contact with the air having a disgustingly sweet odour. (Dissertation H. J. PRINS Delft 1912 p. 160—162).

It may be readily condensed to a colourless, very mobile liquid which solidifies below — 50°.

Liquid dichloroacetylene rapidly combines at — 50° with chlorine tot C_2Cl_6.

The gaseous compound, at least if diluted with H_2 or CO_2, does not seem to be dangerous, but the liquid substance explodes with extreme violence.

Delft, 12 March 1914.

Chemistry. — *"On the Isomorphy of the Ethylsulphates of the Metals of the Rare Earths, and on the problem of eventual morphotropic relations of these salts with analogous salts of Scandium, Indium and Beryllium."* By Prof. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the meeting of March 28, 1914).

§ **1.** In the following paper is given a short review of a comparative study of crystallographical analogies within the series of the *Ethylsulphates* of the metals: *Yttrium, Lanthanium, Cerium, Praseodymium, Neodymium, Samarium, Europium, Gadolinium, Dysprosium, Thulium, Erbium, Neoytterbium, Beryllium, Scandium,* and *Indium*; and also of some *Acetylacetonates* of the three last metals. These investigations were all executed, during the last two years, by means of very small quantities (about 100 to 300 m.G.) of the oxides, which for this purpose were kindly lent to me in the possibly highest degree of purity, by the scientists: Professor G. URBAIN in *Paris*, Sir WILLIAM CROOKES in *London*, and Professor C. JAMES in *Durham, New Hampshire* (U. S. A.). It is an agreeable task to me to thank the above mentioned chemists here once more for their kind help in this matter. The complete description of these investigations will be given in a full paper, which I hope to publish elsewhere [1]) within a short time, with all the data and necessary figures.

§ **2.** This research was started with respect to the question, if it would be possible, to find out any relation between the changes of the crystallographical parameters, which are caused by the substitution of the trivalent atom $Me^{\cdots}$ in the molecule:

$$Me_2^{\cdots} (SO_4 . C_2H_5)_6 + 18\, H_2O,$$

by any other atom of the series of elements here considered, and between the changes in molecular weight, which are simultaneously produced by this substitution. That in general a parallelism of the

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[1]) In the: Recueil des Travaux d. Chim. des Pays-Bas, (1914).

morphotropic influence of a substituent and its atomic weight or atomic volume, may be supposed, is sufficiently proved by the investigations of Mr. TUTTON on the similarly constituted salts (sulphates, selenates, etc.) of the alcali-metals. Possibly it could be stated that within the series of the metals of the rare earths, whose atomic weights differ from each other much less, a quantitative relation of this kind would be found more easily than in the case of the alcali-metals, or in that of other homologous elements of the same group of the periodic system. Moreover, a more detailed investigation of the molecular volumes of those crystallized salts would perhaps give an opportunity to get some information about the parallelism, — not yet sufficiently proved, but too many times advanced, — between the changes of the atomic weights and those of the atomic or molecular volumes of the rare earths or their analogous compounds. Considerations of this kind are moreover closely connected with the already often discussed problem, how far the element *scandium* so widely spread, but isolated only in small quantities and studied too incompletely, must be placed among the metals of the rare earths [1]; finally it could in my opinion hardly be considered superfluous, to compare the crystallographical character of the element *beryllium* once more with that of the metals of the rare earths, in connection with the doubt upon this matter, which has existed during a long time with some crystallographers and chemists. [2]

§ **3**. The choice of the ethylsulphates for these purposes was suggested by the fact, that notwithstanding a number of tentatives with other inorganic and organic acids, till now no derivatives of the above mentioned oxides were obtained, which at the same time fulfilled the following conditions:

a. To have the same number of water-molecules, if hydrated, through the whole series of metals.

b. Not to be efflorescent in dry air, nor to be hygroscopical.

c. To give crystals, whose faces enabled very accurate measurements of the angles, and whose angles showed a sufficient constancy with different individuals of the same salt.

So these conditions are *not* fullfilled: with the beautifully crystallized double nitrates of the bivalent metals Zn, Co, Ni, Mn, and Mg, which always show curved and dull faces, or at least will get them very fast; nor with the platinum double-cyanides or with the

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[1] G. URBAIN, Journ. de Chim. phys. **4**. 32, 232, 321. (1906); URBAIN et LACOMBE, Chem. News **90**. 319. (1904); W. BILTZ, Zeits. f. anorg. Chem **82**. 438. (1913); R. J. MEYER, Zeits. f. anorg. Chem. **86**, 257. (1914).

[2] DEBRAY, Ann. de Chim. et Phys. (3). **44**. 5. (1855); WYROUBOFF, Bull. de la Soc. Minér. de France, **19**. 219. (1896).

sulphates, which differ, like most other salts, in their content of water of crystallisation with the successive elements of the series; etc. Thus my choice was finally fixed on the ethylsulphates; of these only the salts of *thulium* and of *neo-ytterbium* were somewhat difficult to obtain in a measurable form, because of their high solubility and their tendency to form supersaturated solutions. However finally also these salts were obtained in a well developed form.

From the borrowed salts (double nitrates, oxalates, bromates, etc.) first the pure oxides were prepared, then the sulphates, and these finally decomposed in aqueous solution by means of bariumethylsulphate *at a low temperature.* To avoid any strong elevation of temperature as much as possible, the solution was evaporated in vacuo or at a strongly diminished pressure on the waterbath, at temperatures of 22° till 34° C; first the solution must stand for a long time to make the finely divided bariumsulphate precipitate, and to separate it from the mother-liquor by decanting and filtration. Only in this way it was possible, to avoid an admixture of sulphate to the ethylsulphates, formed by hydrolysis of these.

§ **4.** The specific weights of the crystallized salts were determined with the utmost care; I gratefully wish to remember here the valuable assistance of Mr. M. J. Smit, cand. chem., in this tedious work. As well by the pycnometrical method, with orthochlorotoluene as an immersion-liquid, as also by means of heavy liquids (floating-method), we obtained data, which were in full accordance with each other; it need hardly be said, that this was no easy task, regarding the very small quantities of the salts at our disposal.

During this work we found, how far even the purest products of the rare earths, sold in commerce (de Haën, Dr. Drossbach) for scientific purposes, are still removed from the spectroscopical purity of Urbain's preparations and those of the other mentioned scientists. The following determinations of the specific weight may give an impression of this:

Element:	*Specific weight of the pure salts:*	*Spec. weight of the best products in commerce:*
Lanthanium	1,845	1,801
Cerium	1,930	1,839
Praseodymium	1,876	1,848
Neodymium	1,883	1,866
Samarium	1,904	1,884
Gadolinium	1,919	1,905
Ytterbium	2,015	1,857

§ **5.** The following values for the atomic weights of these elements are adopted in this paper: *Yttrium*: 88,6; *Lanthanium*: 139,0; *Cerium*: 140,25; *Praseodymium*: 140,6; *Neodymium*: 144,3; *Samarium*: 150,4; *Europium*: 152,0; *Gadolinium*: 157,3; *Dysprosium*: 162,5; *Erbium*: 167,7; *Thulium*: 168,5; *Neoytterbium*: 172,0; *Beryllium*: 9,1; *Indium*: 114,8; *Scandium*: 44,1.

Of each salt as large a number of crystals as possible was investigated; as many crystals possess more than seventy faces, the total number of measurements is a very considerable one.

Highly remarkable is in first place the *extraordinary variability of external aspect* of the crystals of these yet strictly isomorphous compounds. Every substituting element seems to give some preference to a special aspect in most cases, and under apparently the same circumstances, although eventually *all* the observed forms *can* be present in *all* cases; in the paper to be published at a later period this fact will be discussed in detail.

The crystals are *hexagonal*; a combination of the predominant forms and a stereographical projection of them, are reproduced in fig. 1 and 2.

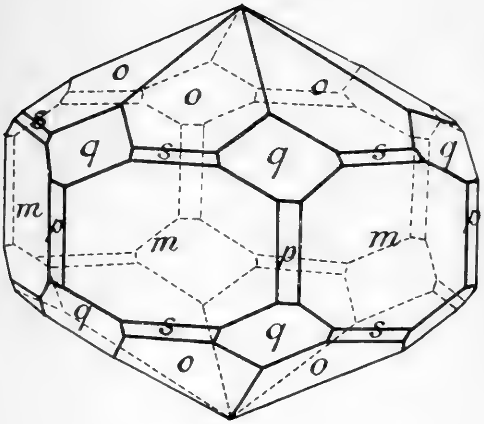

Fig. 1.

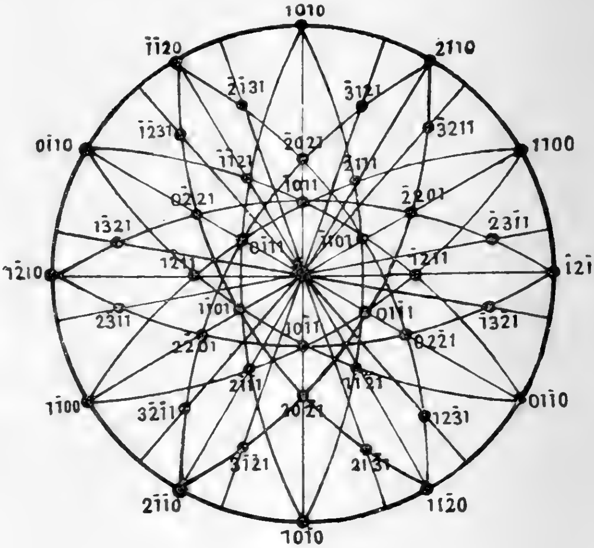

Fig. 2.

Stereographical Projection of the observed crystal forms.

The exact determination of the class of symmetry was only possible by combination of angular measurements and of RÖNTGEN-photography[1]).

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[1]) I was helped in the kindest manner in this work by the valuable assistance of Prof. HAGA and Lecturer Dr. ORNSTEIN, both of this University.

IRON AND INDIUM.

No.	Name		Remarks.	No.
1	*Indium*	y a lue >*v*.	There is *no* relations between these salts and those of the rare earths. Both salts are in all probability directly *isomorphous* with each other.	1
2	*Scandi*			2
3	*Berylli* (Spec. d_4^0=1. salt: B $C_2H_5)_2$	ar- 435. out	There is *no* relation between the crystallonomical character of this salt and the previous ones.	3
4	*Indium*	is en-	These three salts are perfectly isomorphous with each other; the *aluminium*salt is very probably *isodimorphic* with them.	4
5	*Scandiu*	· en-		5
6	*Ferri-*	the *Li-*		6
7	*Berylliu*	the ght; sec- nes ond	There exists *no* relation between the crystallonomical character of this salt and the preceding ones.	7

*) Afte

REVIEW OF THE DATES CONCERNING THE HERE STUDIED SALTS OF BERYLLIUM, SCANDIUM, IRON AND INDIUM.

No	Name of the investigated Salt.	Symmetry.	Parameters	Observed Forms	Optical Properties.	Remarks	
1	*Indium-ethylsulphate*	Monoclinic			Very small axial angle; probably a crossing of the axial planes for blue and red light. Strong dispersion: [illegible]v.	There is *no* relations between these salts and those of the rare earths. Both salts are in all probability directly *isomorphous* with each other	1
2	*Scandium-ethylsulphate*	Monoclinic (probably)					2
3	*Beryllium-ethylsulphate* (Spec. Weight at 25° is: $d_4^{0} = 1.857$; it is a basic salt: $BeO . Be (SO_4 . C_2H_5)_2 + 4 H_2O$	Ditetragonal-bipyramidal	$a : c = 1 : 0.6706$	{001}; {111}; {100}	Optically uniaxial, of negative character; $n_\omega = 1.473$ and $n_e = 1.$[illegible] Very strong birefringence: about 0.04	There is *no* relation between the crystallonomical character of this salt and the previous ones	
4	*Indium-acetylacetonate*	Rhombic-bipyramidal	$a : b = 0.5593 : 1$	{110}; {010}; {001}	The plane of the optical axes is {100}; small axial angle; birefringence: +; dispersion: $\rho < v$.	These three salts are perfectly isomorphous with each other; the *aluminium*salt is very probably *isodimorphic* with them.	4
5	*Scandium-acetylacetonate*	Rhombic-bipyramidal	$a : b = 0.5621 : 1$	{001}; {110}; {010}	The plane of the axes is {100}. Very small axial angle; birefringence: +; dispersion: $\rho < v$.		5
6	*Ferri-acetylacetonate*	Rhombic-bipyramidal	$a : b = 0.5689 : 1$ $b : c = 1 : 1.2225$ *)	{001}; {110}; {021}; {011}	Plane of the optical axes is {100}; the axial angle is about 50°, for *Li*-light; negative birefringence.		6
7	*Beryllium acetylacetonate*	Monoclinic-prismatic	$a : b : c = 1.4765 : 1 : 1.3592$ $\beta = 52°20'$	{010}; {001}; {100}; {110}; {210}, {101}; {211}	Very remarkable dispersion of the axial planes for blue and red light; very strong dispersion of all bisectrices. The crossing of axial planes and the change of first and second bissectrices for different wave-lengths, is very characteristic.	There exists *no* relation between the crystallonomical character of this salt and the preceding ones	7

*) After measurements of V. VON LANG.

H-METALS.

Indices.	Remarks.	No.
$n_e = 1.480$	Almost colourless	1
$n_e = 1.473$	Colourless crystals	2
$n_e = 1.474$	Colourless crystals	3
$n_e = 1.479$	Emeraldgreen cryst.	4
$n_e = 1.479$	Pink crystals	5
$n_e = 1.481$	Pale yellow crystals	6
$n_e = 1.484$	Colourless	7
$n_e = 1.482$	Colourless crystals	8
$n_e = 1.482$	Colourless crystals	9
$n_e = 1.480$	Pale rosa crystals	10
$n_e = 1.486$	Colourless	11
$n_e = 1.483$	Colourless	12

hich salt was better crystallised than
measurable needles The other data
d crystals also from the oxide of M.

nations with the often recrystallised

TABLE OF SOME DATA, RELATING TO THE ETHYLSULPHATES OF THE RARE EARTH-METALS.

No.	Name of the Element, whose salt is investigated.	Axial Ratio.	Observed Forms.	Specific Weight (at 25° C.)	Molecular Volume.	Topic Parameters.	Refractive Indices.	Remarks.	No
1	*Yttrium*	1:0.5035	$\{10\bar{1}0\}$; $\{11\bar{2}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$; $\{20\bar{2}1\}$.	1.764	709.80	6.4737:6.5190	$n_0 = 1.493; n_e = 1.480$	Almost colourless	1
2	*Lanthanium*	1:0.5073	$\{11\bar{2}0\}$; $\{10\bar{1}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$; $\{20\bar{2}1\}$; $\{21\bar{3}1\}$; $\{31\bar{2}1\}$.	1.845	733.27	6.5279:6.6231	$n_0 = 1.482; n_e = 1.473$	Colourless crystals	2
3	*Cerium*	1:0.5075	$\{10\bar{1}0\}$; $\{11\bar{2}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$; $\{20\bar{2}1\}$.	1.930	702.27	6.4337:6.5303	$n_0 = 1.482; n_e = 1.474$	Colourless crystals	3
4	*Praseodymium*	1:0.5058	$\{10\bar{1}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$.	1.876	722.86	6.5033:6.5787	$n_0 = 1.486; n_e = 1.479$	Emeraldgreen cryst.	4
5	*Neodymium*	1:0.5068	$\{10\bar{1}0\}$; $\{11\bar{2}1\}$; $\{10\bar{1}1\}$.	1.883	724.10	6.5026:6.5911	$n_0 = 1.487; n_e = 1.479$	Pink crystals	5
6	*Samarium*	1:0.5072	$\{11\bar{2}1\}$; $\{10\bar{1}0\}$; $\{10\bar{1}1\}$.	1.904	722.52	6.4961:6.5897	$n_0 = 1.490; n_e = 1.481$	Pale yellow crystals	6
7	*Europium*	1:0.5058	$\{10\bar{1}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$.	1.909	722.31	6.5016 6.5770	$n_0 = 1.494; n_e = 1.484$	Colourless	7
8	*Gadolinium*	1:0.5050	$\{10\bar{1}0\}$; $\{11\bar{2}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$.	1.919	724.07	6.5103:6.5753	$n_0 = 1.490; n_e = 1.482$	Colourless crystals	8
9	*Dysprosium*	1:0.5050	$\{10\bar{1}0\}$; $\{10\bar{1}1\}$; $\{11\bar{2}1\}$.	1.942	720.85	6.5007:6.5657	$n_0 = 1.495; n_e = 1.482$	Colourless crystals	9
10	*Erbium*	1:0.5053	$\{10\bar{1}1\}$; $\{11\bar{2}1\}$; $\{10\bar{1}0\}$; $\{11\bar{2}0\}$; $\{21\bar{3}1\}$; $\{31\bar{2}1\}$; $\{20\bar{2}1\}$.	1.907	739.6	6.5553:6.6247	$n_0 = 1.490; n_e = 1.480$	Pale rosa crystals	10
11	*Thulium*	1:0.5044	$\{10\bar{1}0\}$; $\{10\bar{1}1\}$; $\{21\bar{3}1\}$; $\{11\bar{2}0\}$; $\{11\bar{2}1\}$.	2.001	705.59	6.4494:6.5293	$n_0 = 1.492; n_e = 1.486$	Colourless	11
12	*Neoytterbium**)	1:0.5079	$\{10\bar{1}0\}$; $\{11\bar{2}1\}$; $\{10\bar{1}1\}$; $\{11\bar{2}0\}$; $\{20\bar{2}1\}$.	2.019	702.76	6.4407:6.5207	$n_0 = 1.497; n_e = 1.483$	Colourless	12

*) The axial ratio and the limiting faces were determined with a salt prepared from a product of commerce, which salt was better crystallised than the pure neo-ytterbiumsalt, which allways was deposited from very supersaturated solutions like small, not well measurable needles The other data sub 12 however, are all determined with the pure neo-ytterbiumsalt. Finally we obtained some well developped crystals also from the oxide of M. JAMES; the measurements gave the same results, as they are reproduced here in the table.

A remarkable fact is the anomalous value of d_4 with the *cerium*salt; however in many repeated determinations with the often recrystallised substance, the same abnormality was every time recorded.

For the measurements of the angles enabled us only to state, that a hexagonal or dihexagonal symmetry was present; the RÖNTGEN-pattern however, obtained by radiation through a crystalplate, cut perpendicularly to an optical axis, showed immediately, that no binary axes of symmetry, nor vertical symmetry-planes were present. Therefore the true symmetry of the crystals could only be that of the *hexagonal-bipyramidal* or of the *hexagonal-pyramidal* (hemimorphic) class. The external aspect of the crystals could bring no decision in the choice between these two possibilities; the fact, that the faces at both ends of the vertical axis showed always about the same degree of development, could perhaps be considered as a very weak argument for the view, that *no* polarity of the vertical axis were really present, and thus a single horizontal symmetry-plane must necessarily exist. However the figures of corrosion which were obtained on the faces of the prism $\{10\bar{1}0\}$ by heating for a short time the crystals

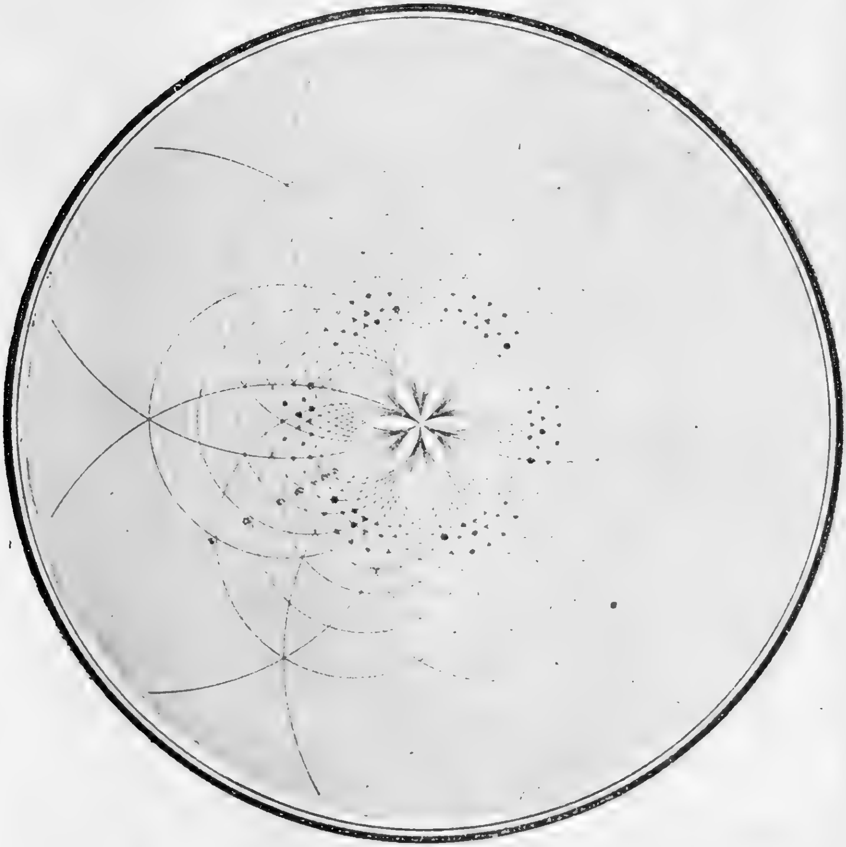

Fig. 3.

Stereographical projection of the diffraction-pattern of the Erbium-aethylsulphate ($\perp$ opt. axis) obtained by RÖNTGEN-rays.

of the *yttrium*salt in their saturated mother-liquor, showed without any doubt, that such a horizontal plane of symmetry is really present. Thus all these salts belong to the *hexagonal-bipyramidal* (hemiëdric) class of the hexagonal system.

A stereographical projection of the pattern, produced by the RÖNTGEN-rays (*erbium*salt), is reproduced in fig. 3; the differences in intensity of the dark spots on the photographic plate, are indicated here by means of larger and smaller dots. [1])

Commonly the crystals are tabular parallel to two opposite faces of the vertical prism; they make thus the impression of hexagonal plates. The most interesting data are summarized in the subjoined table.

§ **6.** In the first instance this review of the obtained dates shows clearly, that all these salts of the metals of the rare earths belong to a series of *perfectly isomorphous* substances. Moreover it has been proved by a great number, — i.e. several thousands, — of exact measurements, *that the deviations of the angles from the main value with the different individuals of a same crystalspecies, must be considered to be of the same order as the deviations of the main values of corresponding angles with the successive terms of the whole series.* Thus we can consider all those salts to have *practically the same crystalform*, whose parameters oscillate about the most probable main value:

$$a : c = 1 : 0{,}5062 \pm 0{,}0012$$

with deviations, which cannot be considered as typical for each kind of crystals separately. Therefore the differences of the molecular distances in the corresponding space-lattices of these crystals, can be only of the same order, as the differences in *molecular volumes* with the successive terms of the series. It must be considered a remarkable fact in this respect, that, although the specific weights of these salts are, generally speaking, gradually increasing with the increase of atomic weight of the rare earth-metals — (with the exception of the *erbium*-salt, which was prepared from not highly pure oxide, and of the *cerium*-salt, whose isolated position in this respect seems to be a real fact) — these molecular *volumes*, and just so the calculated topic parameters, show a very evident *periodicity*. [2]) This fact, which may be graphically represented in fig. 4

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[1]) The stereographical projection is made upon a circular base, with a radius of *twice* the distance between crystalplate and RÖNTGEN-tube.

[2]) These topic parameters are calculated for the regular triangular prism

and 5, may lead to the suspicion, that the *atomic volumes* of the

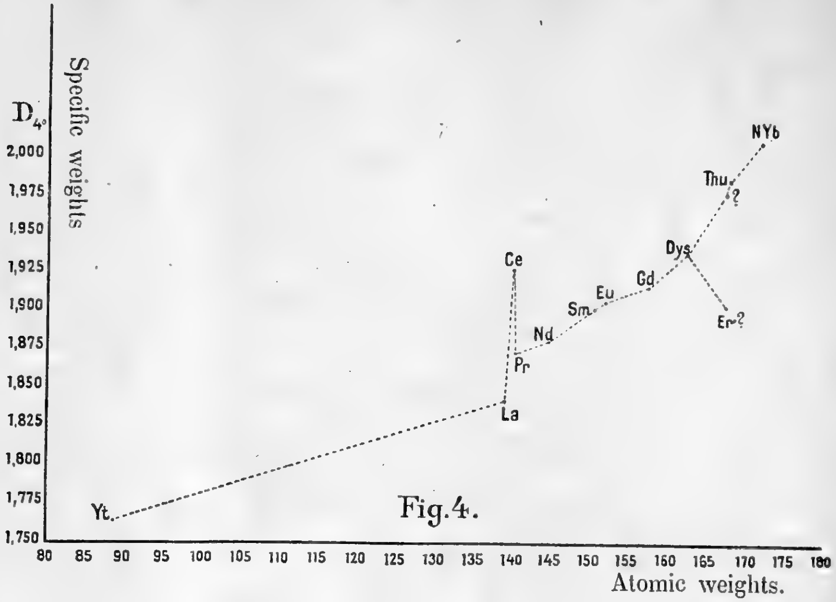

Fig. 4.

mutually substituting elements in these salts, can no longer be considered as gradually increasing with the increase of the atomic weights within this series of elements, if no better proof of this view is brought forward than has been done up to this date. Possibly more detailed accurate research with spectroscopically pure materials, and extended over all terms of this remarkable group of elements, would prove with full evidence, that the atomic-volume-curve of LOTHAR MEYER and MENDELEJEFF possesses also a single or double *periodicity* within the group of the rare earth-metals.

That this fact was not shown previously in any clear way, may be caused by the extreme difficulty of getting these elements in an absolutely pure state. For they will form within the whole series solid solutions with each other in all proportions; and as is well-known from RETGERS' investigations, the specific volume of such mixed crystals will be in general continuously variable with their chemical composition, and will be calculable in most cases from a linear function of this composition and the specific volumes of the pure components.

(*Bravais*) as "unit" of the space-lattice, from the relations:

$$\tfrac{1}{2}\chi = \frac{\left(\frac{V}{c}\right)^{1/3}}{2\,sin\,60°} \quad \text{and} \quad x = \frac{(Vc^2)^{1/3}}{sin\ 60°}.$$

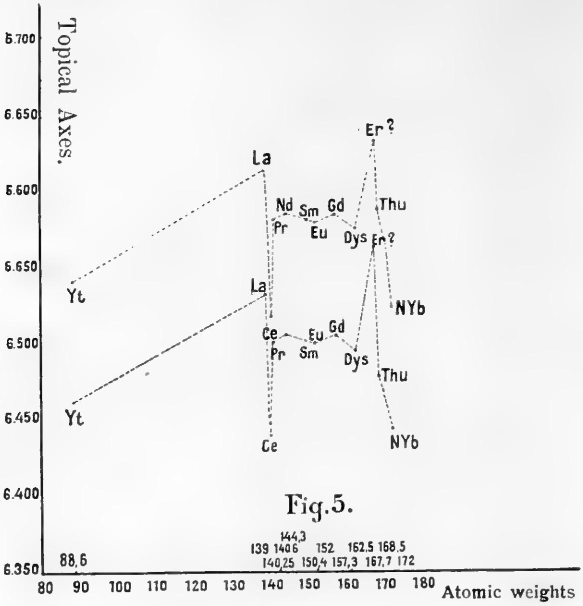

Fig. 5.

And even if this is not always the case, it must be clear, that with chemically not quite homogeneous material, there will be found quantitative data, from which must follow other relations between different properties, as they would follow from observations with absolutely pure substances.

Moreover the available data considering specific weights of corresponding derivatives of the rare earth-metals, are highly rudimentary and not very trustworthy, as will be shown later in the full paper on these investigations. With respect to the available data it can hardly be justified to suppose a general parallelism between atomic weights and atomic volumes within this group of homologous elements.

I may remind readers of the fact, that in a somewhat different train of thought Mr. URBAIN has shown just such a kind of periodicity to exist with his spectroscopically pure oxides, with respect to some other properties. He was able to show [1]), that the *coefficients of magnetisation* μ of the oxides of these metals, determined after the method of CURIE and CHENEVEAU, and compared with the value of μ of pure cobaltsulphate: $CoSO_4$, $7\,H_2O$, were ($\times 10^{-6}$):

for:	*Nd*	*Sm*	*Eu*	*Gd*	*Tb*	*Dys*
	33,5	6,5	33,5	161	237	290

while these numbers are *decreasing* continually, passing *holmium* with a not yet known, but probably very great value of μ, over *erbium*,

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[1]) URBAIN et JANTSCH, Compt. rend. **174**. 1286. (1908).

thulium, *neoytterbium* and *lutetium*. On the other side however, *lanthanium* is diamagnetic, while *praseodymium* possesses a greater value for μ than *neodymium*. Thus the curve, showing the dependence of μ upon the atomic weight, must possess *two maxima*: one in the *cerium*-group, and the second, much steeper maximum, in the *yttrium*-group.

There also exists such a periodicity in the *basic properties* of these oxides; these seem to decrease from *lanthanium* to *terbium*, then to increase with *holmium* (*yttrium*) and *erbium*, and again to decrease to the side of *neoytterbium*; the elements are arranged in order of increasing solubility of their ethylsulphates:

$$— La \begin{matrix} Ce \\ Pr \end{matrix} Nd\ Sm\ (\textit{Cerium}\text{-group}),$$

and: *Eu Gd Tb Dys Ho Yt Er Thu N-Yb* (*Yttrium*-group)

An analagous periodicity seems to exist also for the solubility of other salts of these metals, e.g. for the *oxalates*, etc.

Finally all these facts may persuade us to some extent, that it is really not at all justifiable, to deny the possibility of such a periodicity a priori, even with respect to the relation between atomic weight and volume, without accurate and extended investigations with *absolutely pure* material; on the contrary: the facts here published can be used as strong arguments in favour of the view of the existence of such a periodical relationship. ¹)

§ **7.** Now some more data about analogous investigations with *scandium*-, *beryllium*- and *indium*-salts may find a place here. Originally tentatives were made, to reach our scope also by means of the study of the ethylsulphates. We succeeded in obtaining from *scandium*-, and *indium*-oxide, the corresponding ethylsulphates in the form of

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¹) In connection with this I may remark once more, that an analogous abnormality in the molecular volumes of the *double nitrates* of these same oxides of URBAIN, was found a short time ago by JANTSCH: Zeits. f. anorg. Chemie **76**, 303, (1914)), with the salts of *praseodymium* and *neodymium*: the last compounds always possess the greater molecular volume.

Moreover another argumentation for such a periodicity of properties within this group of elements, can be derived from the available data of *meltingpoints* of these metals or of their analogous compounds. For MUTHMANN and WEISS (Lieb. Ann. **331**. 1. (1904)) stated, that the meltingpoint of *La* is: 810° C.; of *Ce*: 623° C.; of *Pr*: 940° C.; of *Nd*: 840° C. In the same way BOURION (Ann. de Chim. et Phys. (8) **20**. 547, (1910), showed, that the meltingpoints of the *chlorides* are: of $LaCl_3$: 890° C.; of $CeCl_3$: 848° C; of $PrCl_3$: 810° C.; of $NdCl_2$: 784° C.; of $SmCl_3$: 686° C.; of $GdCl_3$: 628° C.; of $TbCl_3$: 588° C., but on the contrary, for $DysCl_3$: 680° C., — being thus about 100° *higher*.

well-crystallized preparations; however these crystals had microscopical dimensions and were only little adapted for goniometrical measurements, because they were intergrown with each other in a chaotic mass. However it was possible to prove, that *no* relation in the crystallographical architecture of these crystals with that of the ethylsulphates of the also trivalent rare earth-metals exists. These salts are of monoclinic symmetry, and they possess characteristic optical properties, which can be considered as most typical for them. In the subjoined table the principal data are put together.

From this review it follows, that the *beryllium-ethylsulphate* evidently must be placed in an isolated place, with respect to all other ethylsulphates. It is tetragonal and possesses a very deviating chemical composition, being a *basic* salt of the formula: $BeO. Be(SO_4.C_2H_5) + + 4H_2O$; analysis gave: 14,3°/$_0$ BeO.

§ **8.** Because evidently the above mentioned salts of *indium* and *scandium* were little adapted for measuring purposes, the corresponding *acetylacetonates* were prepared. The acetylacetonates of the metals of the rare earths crystallise always like felty, fine needles, which are not exactly measurable. On the contrary, the acetylacetonates of the trivalent metals: *scandium, aluminium, indium* and *iron* crystallise in big, flat crystals, which immediately show themselves closely related to each other, but widely different from the salts of the first mentioned series. The measurements really prove, that the salts of *scandium, iron,* and *indium* are directly isomorphous with each other, while the *aluminium*salt must stand to them in the relation of *isodimorphy*. With the trivalent *gallium*, all those metals must therefore be placed into the same group; evidently they are *not* immediately related to 'the rare earth-metals. Thus also the question, if the element *scandium* must be placed among the rare earth-metals, can be answered in the *negative*, as well with respect to arguments formerly adduced from several sides, as with respect to the facts described here ¹).

The *beryllium-acetylacetonate* is monoclinic, and, generally speaking, very widely different from the other acetylacetonates. This substance is a highly remarkable object for optical demonstrations: with enormous values for its dispersion, it shows the phenomenon of the crossing of axial planes, like the mineral *brookite*; but in agreement with the monoclinic symmetry, the effect of the dispersion of the

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¹) See about this question however the just published paper of R. J. Meyer, (loco cit.). In my opinion the claimed analogy (p. 268) between *scandium* and *yttrium* can hardly be defended in a persuading way.

bisectrices for different wave-lengths is here superposed upon it. In this way a highly remarkable combination of crossed and horizontal dispersions results from it, while the orthodiagonal is for some wave-lengths the direction of the first bisectrix, for other ones that of the second bisectrix. The very peculiar optical phenomena resulting from this, will be described in detail and explained in the paper to be published lateron.

Laboratory for Inorganic and Physical Chemistry
of the University.

Groningen, 14 March 1914,

Paleontology. — *"Contribution to the knowledge of the genus Kloedenella,* ULRICH *and* BASSLER." By J. H. BONNEMA. (Communicated by Prof. J. W. MOLL.)

(Communicated in the meeting of March 28, 1914).

When examining an erratic boulder, consisting of Chonetan or Beyrichian limestone and originating from Vollenhove, I found some remains of Ostracoda which, I presumed, originated from the genus which KRAUSE has called *Beyrichia hieroglyphica* [1]), of which besides an illustration (fig. 1) he gave the following description:

Beyrichia hieroglyphica n. sp.

Länge 0,74 mm. Höhe 0,5 mm.

Die Schale ist annähernd rechteckig mit geradem Dorsal- und Ventralrand und gerundeten Seitenrändern. Auf der Schalenoberfläche befinden sich 5 symmetrisch angeordnete grubenförmige, durch schmale Leisten von einander getrennte Vertiefungen, je eine parallel den beiden Seitenrändern vom Dorsalrande bis zum Ventralrande verlaufend, in der Mitte zwischen diesen eine kürzere, welche vom Dorsalrande bis zur Mitte der Schale reicht, und unterhalb derselben zwei rundliche Gruben am Ventralrande.

Die Art weicht von allen anderen Beyrichien unserer Geschiebe weit ab. Am nächsten scheint sie noch der *Beyrichia Halli* JONES aus der Waterlime-Gruppe von Utica N. Y., zu stehen, nur dass bei dieser die beiden unter der centralen Furche befindlichen Vertiefungen fehlen.

Ich fand die eben beschriebene Form in einem grauen, fleckigen Geschiebe zusammen mit *Beyrichia Wilckensiana, B.* aff. *Kloedeni,*

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[1]) Zeitschr. d. deutsch. geol. Gesellsch., XLIII, p. 506, Taf. XXXII, Fig. 10, 1891.

Cypriden und Fischresten. Die einzelnen Schalen waren nur in Bruchstücken aus dem Gestein zu lösen. Fig. 10 ist ein ergänztes Bild eines der best erhaltenen Exemplare."

In order to ascertain whether the remains of Ostracoda which I had found, really originated from the genus described by KRAUSE as *Beyrichia hieroglyphica,* I looked for similar remains in an erratic boulder consisting of Chonetan or Beyrichian limestone which I had found some time ago when a pond was being dug near a villa, called Hilghestede, between Groningen and Haren. This erratic boulder is now in the collection of the Mineralogical Geological Institute of the University of Groningen. I was then fortunate enough to find not only a great number of separate valves, but also several complete carapaces.

This latter erratic boulder is a dark grey somewhat crystalline piece of Beyrichian limestone, in which among other things I found: fish-remains, *Kloedenia Wilckensiana* JONES, *Beyrichia protuberans* BOLL, *Beyrichia tuberculata* KLÖDEN sp. and *Leperditia phaseolus* HIS. The first three fossils had also been found in the erratic boulder in which KRAUSE found remains of *Beyrichia hieroglyphica,* if at least *B.* aff. *Kloedeni* may be identified with *Beyrichia protuberans,* which seems almost certain [1]).

It appeared to me that the illustration given by KRAUSE represents a left valve, as the posterior of the two little furrows is always the bigger one (the anterior may even be absent). This figure, however, is very incomplete, for this author seems to have been ignorant of the fact that the remains found by him, had only partly been uncovered. Before the anterior lobe there is another sickle-shaped, less convex part and behind the posterior lobe a similar part tapering towards the lower end. The narrow inferior ends of the less convex parts meet at the ventral side.

The lobe along the ventral edge, which joins the other lobes, is nearly straight and not curved, as represented by KRAUSE; in his description, however, he calls it straight. The ventral edge of the carapaces is concave.

As the most striking feature of this Ostracod I found, however, that in the left valve the two anterior lobes unite at the top into a process, which lies in a notch of the right valve (figs. 3 and 4). No doubt the great number of complete carapaces which were found, is due to this arrangement.

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[1]) Wissenschaftliche Beilage zum Programm der Luisenstädtischen Oberrealschule zu Berlin. Ostern 1891, Berlin, R. Gaertners Verlagsbuchhandlung (HERMANN HEYFELDER). p. 12.

J. H. BONNEMA: "Contribution to the knowledge of the genus Kloedenella, Ulrich and Bassler."

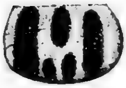

Fig. 1.
Left valve of *Kloedenella hieroglyphica* A. Krause sp. (After Krause). 20 ×.

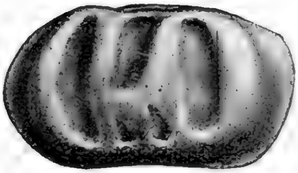

Fig. 2.
Kloedenella hieroglyphica A. Krause sp. Left side view of complete carapace. 40 ×.

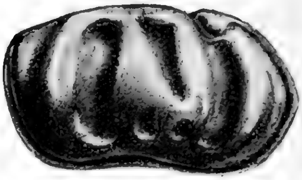

Fig. 3.
Kloedenella hieroglyphica A. Krause sp. Right side view of complete carapace 40 ×.

Fig 4.
Kloedenella hieroglyphica A. Krause sp. Dorsal view of complete carapace. 40 ×.

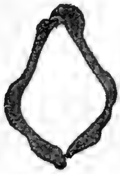

Fig. 5.
Transverse section of a carapace of *Kloedenella hieroglyphica* A Krause through the part of the muscle impression, as seen from behind. 35 ×.

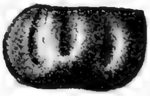

Fig. 6.
Left valve of *Kloedenella Hallii* Jones. × 15. (After Jones).

Fig. 7.
Kloedenella pennsylvanica Jones sp. Left side, end and ventral views of complete carapace, 15 ×. (After Jones).

Proceedings Royal Acad. Amsterdam. Vol. XVI.

For the rest the hinge line is straight. Along the straight part the right valve overlaps the left one. By making sections of complete carapaces (fig. 5) I found that the sharp hinge line of the left valve lies in a deep furrow of the right one.

On the other hand the free edges of the right valve are sharp and when the carapaces are closed, these sharp edges lie in a furrow on the free edges of the left valve. So the left valve overlaps the right one except along the hinge line (fig. 2).

In the lower part of the middle-most of the three larger furrows each valve has a round spot indicating the place where the adductor was fastened.

When I had become better acquainted with *Beyrichia hieroglyphica* KRAUSE, the resemblance between this Ostracod and *Beyrichia Hallii* JONES [1]) (fig. 6), to which KRAUSE drew the attention, proved much greater than the latter could presume. Another thing that struck me was that in the valve represented by JONES as a right one — though in fact it is a left one — the two front lobes also seem to join into a process. In order to see in how far I was right in my supposition I applied to Dr. BASSLER, curator of the National Museum of Washington, with the request to send me some material of this Ostracod. This was kindly sent to me and I saw that the two anterior lobes on the left valve of *Beyrichia Hallii* JONES indeed unite dorsally into a process, similarly to those in *Beyrichia hieroglyphica* KRAUSE.

On further examining the literature I found that ULRICH and BASSLER [2]) had classified *Beyrichia Hallii* JONES among their genus *Kloedenella,* of which they call the underdevonian *Kloedenella pennsylvanica* JONES (fig. 7) a typical representative.

Then I asked DR. BASSLER to send me some material of this latter Ostracod. In the complete carapace of *Kloedenella pennsylvanica,* which was then sent me, I found the same characteristic way of connecting the two valves, which is no doubt also found in other Ostracoda, for which the two authors mentioned above have instituted a new genus *Kloedenella,* for they make special mention of the fact that of most of the representatives complete carapaces have been found.

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[1]) The Quatérly Journal of the geological Society of London, Vol. XLVI, p. 15, Pl. IV. fig. 21. 1889.

JONES has called this Ostracod *B. Hallii* and not *B. Halli* as KRAUSE writes.

[2]) N⁰. 1646. — From the Proceedings of the United States National Museum. Vol. XXXV. p. 317.

Of the genus *Kloedenella* Ulrich and Bassler give the following diagnosis:

"Carapace small, strongly convex, elongate, somewhat barrel-shaped, the length usually less than 1.5 m.m., dorsal edge nearly straight, ventral edge usually somewhat concave, ends approximately equal in height but differing in outline, the antero-dorsal angle often rectangular and always more distinct than the post-dorsal. Valves unequal, the right overlapping the left around the ends and the ventral side. Of the lobation the constant features are two sharply impressed vertical or slightly oblique furrows, separated by a narrow lobe, in the posterior half. In the more simple forms these furrows extend only about half across the valve. Anterior half may be uniformly convex, but, as a rule, is more or less clearly bisected vertically by a straight or curved furrow. When present, this anterior furrow often produces an appearance suggesting the "loop" of a *Bollia*. Surface generally smooth and polished and without ornamental markings".

Here the following remarks are to be made: first, that the way in which the two valves are connected in *Kloedenella hieroglyphica* Krause, as well as in *Beyrichia tuberculata* Klöden and *Primitia Tolli* Bonnema, proves that what Ulrich and Bassler called the posterior end is to be looked upon as anterior.

Secondly "dorsal edge nearly straight" ought to be replaced by "Both valves have a straight dorsal edge, the sharp dorsal edge of the left valve lies in a furrow on the dorsal edge of the right valve. On the left valve there is a process before the right dorsal edge, which fits into a notch of the right valve."

To "valves unequal" may be added that the right valve overlaps the left along the hinge-line. This is at least also the case with *Kloedenella pennsylvanica* as well as with *Kloedenella hieroglyphica*.

The criteria of the genus *Kloedenella* are accordingly:

Carapace elongate and small, the length usually less than 1.5 m.m., posterior half very convex, dorsal edge nearly straight, ventral edge usually somewhat concave, ends equal in height, anterior edge uniformly curved and passing almost invisibly into dorsal edge, forming a very obtuse angle with it; posterior edge less curved, forming a nearly rectangular angle with the dorsal edge. Valves unequal, the anterior half of the right valve has a notch in which a process of the left valve lies; this latter is located before the straight sharp hinge line, which is situated in the furrow on the straight hinge line of the right valve. The right valve overlaps the left along the hinge line. The sharp free edges of the right valve lie in a furrow on the free edges of the left valve so that the left valve overlaps the right along the free edges.

The surface of the carapaces is different, though furrows and lobes are always present. Constant features on the anterior half of the valves are two more or less vertical furrows, separated by a narrow lobe. The posterior half may also have a furrow. Else the surface is generally smooth and without ornamental markings.

As may have been inferred from the above statements, the position which I have given to this Ostracod corresponds to the position which in my opinion [1] is due to *Beyrichia tuberculata* KLÖDEN sp., in which there is a furrow on the free edges of the left valve, whereas the right has sharp edges. From Dr. BASSLER of Washington I received a letter the other day, in which he stated that he and Dr. ULRICH considered as posterior what I had assumed as the anterior end in *Primitia Tolli* BONNEMA, *Beyrichia tuberculata* KLÖDEN sp. and *Beyrichia protuberans* BOLL; but to this I cannot possibly agree. Their opinion is based on the fact that the lower of the two nodes situated at one of the two ends, which in some valves of *Beyrichia tuberculata* has widened into an "ovarian pouch", would be situated in the anterior half in the position suggested by me, whereas in recent Ostracoda this node is found in the posterior half. In my opinion, however, they disregard the fact that in the position accepted by them, the eyes would be situated at the posterior end of the animal, which seems very unlikely. They call upon me to prove that the "ovarian pouch" has been at the anterior end in paleozoic Ostracoda. I think I have sufficiently proved this with my investigations into the location of the eyes.

Next I want to state that what ULRICH and BASSLER called "ovarian pouch" has to be considered as an incubation pouch, and like KIESOW I have no objection to assume that in the paleozoic Ostracoda this was located in the anterior half of the carapace, whereas in the recent *Cythere gibba* MÖLL. it is situated in the posterior half of the carapace but near the centre.

Finally I tender my best thanks to Mr. BOTKE, teacher in the "Middelbare Landbouwschool" (Secondary Agricultural School) of Groningen, who has been kind enough to make the drawings of *Kloedenella hieroglyphica* KRAUSE sp., necessary for this paper.

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[1] These Proc. **16**, 1913, p. 67–74.

Physics. — *"The effect of temperature and transverse magnetisation on the continuous-current resistance of crystallized antimony."* By Dr. W. J. DE HAAS. Communication from the BOSSCHA-laboratory. (Communicated by Prof. DU BOIS).

(Communicated in the meeting of March 28, 1914).

Introduction. There exists an extensive literature on the effect of transverse magnetisation on the electric conductivity of different metals and metalloids. We may divide these into three groups i.e. 1. ferromagnetic, 2. paramagnetic, 3. diamagnetic substances. Other phenomena also suggest this grouping.

As to our effect, the substances mentioned in section 1 show distinctly measurable changes in the resistance. Those mentioned in sect. 2 however have been less investigated and until now give only exceedingly small effects[1], the nature of which is very difficult to determine. In contrast with the HALL-effect, the ferromagnetic and diamagnetic substances show in our case a change in the resistance which is dependent on the direction of the field. For ferromagnetic substances a decrease and an increase of the resistance have been observed, while also the sign is dependent on the temperature[2]) at least for Swedish iron.

By far the most measurements have been made with conglomerates.

The diamagnetic substances on the contrary always show an increase of resistance with the temperature, not a change of this increase into a decrease. The curves, which represent the resistance as a function of the field have all the same character; sometimes the effect is very large. For example for bismuth in a field of 37 K.G. at —190° C. $R'/R = 230$[3]) and at hydrogen temperatures in a field of 17 K.G. $R'/R = 380$[4]), while for graphite in a field of 40 K.G. and at the temperature of liquid hydrogen $R'/R = 130$[5]). Until now the diamagnetic elements have been investigated; bismuth[6]), antimony[7]), carbon[8]) tellurium[9]) gold[10]), silver[11]), copper[12]), zinc[13]) lead[14]), cadmium[15]), mercury[16]).

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[1]) L. GRUNMACH and F. WEIDERT, Ann d. Phys. **22**, p. 141, 1907.

[2]) H. KAMERLINGH ONNES and B. BECKMAN, Comm. Leiden **12** N⁰. 132*a*, 1912.

[3]) H. DU BOIS and A. P. WILLS, Verh. d. D. Phys. Ges. **1**, p. 169, 1899.

[4]) H. KAMERLINGH ONNES, Comm. Leiden, **12** N⁰. 129, 1912.

[5]) D. E. ROBERTS, Ann. d. Phys. **40**, p. 453, 1913

[6]) F. C. BLAKE, Ann. d. Phys. **28**, p. 449, 1909.

[6]) [10]) [12]) [16]) H. KAMERLINGH ONNES and BENGT BECKMAN, Comm. Phys. Labor. Leiden **12** N⁰. 129, 130, 1912.

[7]) A. v. ETTINGSHAUSEN, Wien. Akad. Ber. **59**, p. 714, 1887.
PH. LENARD, Wied. Ann. **39**, p. 637, 1890.

[10]) [11]) [12]) [13]) [14]) [15]) L. GRUNMACH and F. WEIDERT, loc. cit.

[15]) [13]) [8]) [16]) [12]) [10]) [11]) J. PATTERSON Phil. Mag. (6) **3**, p. 643, 1902.

[9]) [15]) [13]) [10]) C. W. HEAPS, Phil. Mag. (6), **24**, p. 813, 1912, VI. **22**, p. 900. 1911.

[8]) [13]) [15]) S. C. LAWS, Phil. Mag. (6) **19**, p. 694, 1910.

A list of the literature on bismuth up till 1909 can be found in a paper by F. C. BLAKE [1]). Of the more recent experiments must be mentioned those of KAMERLINGH ONNES and BECKMAN [2]), who worked at temperatures down to — 258° C. Carbon has been investigated by ROBERTS, who also gives the literature.

There remains to be mentioned, that researches on crystallized specimens have been made in the Leyden laboratory on bismuth and by ROBERTS on graphite. These are very important, as the orientation of the principal axis has a great influence on the effect. It is principally from this side that we can expect some light on the otherwise unnecessarily complicated phenomena. However crystals have been investigated insufficiently. A method to obtain large metal crystals would certainly be of great use. So far reasonably large crystals have only been made with bismuth.

§ 1. Investigation of antimony.

We shall use the following notations.

R' Resistance in the field,

$R'/\!/$ Resistance in the field, when the axis of the crystal is parallel to the field,

$R'\perp$ The same with the axis perpendicular to the field,

R Resistance without a field, while the index at the foot indicates the temperature, at which the measurements have been made,

$\mathfrak{H}$ field.

Out of several antimony crystal conglomerates of MERCK the best specimens were selected; the material seemed to be very pure and according to the analysis contained less than $^1/_{10000}\,^0/_0$ iron. The pieces were split into thin plates along the basic planes, which were at the same time planes of perfect cleavage. These plates were then immersed in shellac and carefully polished into small rods. At both the ends of one of these rods (long 4 mm, broad 0.55 mm, thick 0.15 mm) two copperwires were soldered. These wires, were carefully insulated with shellac, and the two at one end were bent over the rod so that they came into the same direction as the other two. Then the whole, wires and rods, was slipped into a cylindrical glass tube of 0.8 mm diameter. The wires were then pulled through a brass capillary, in the end of which the tube was fitted. Perpendi-

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[1]) F. C. BLAKE, Ann. d. Phys. 28, p. 449, 1909.

[2]) l. c.

cular to the brass capillary a needle was soldered. When the apparatus was mounted, so that it could be rotated, the needle passed a fixed scale, indicating in this way the orientation of the crystal axis in the field. The resistances were measured with a THOMSON bridge. As this method requires wire resistances small compared with the fixed resistance, in the arms of the bridge (110 ohms in each arm), the above mentioned wires, which were of necessity thin because the four of them had to pass through the glass and brass capillary, were kept as short as possible. When they had left the brass capillary they were soldered to very thick wires, leading to the bridge.

In the bridge a galvanometer of the type of DU BOIS and RUBENS was used. The magnet most used was a small half ring magnet of the newest type with water cooling. For some determinations a large model magnet was used. This new type enables a long series of measurements to be made without introducing an error due to rise of the temperature in the field.

For the resistance measurements at the temperature of liquid air the newly constructed vacuum cryoarmature on the immersion principle has been very useful [1]). In fact the combination of the strong fields up to 45 K.G. with low temperatures can easily be obtained; the field was only very slightly diminished by the gaps in the pole pieces in which the DEWAR vessel fitted. This strong field is partly due to the use of ferrocobalt for the pole pieces.

The magnetic field was measured by the usual ballistic method; nothing particular has to be remarked on this subject. For the estimation of the influence of the low temperatures on the field between the ferro-cobalt pieces the DEWAR vessel with the liquid air was quickly taken away and immediately afterwards the field was measured. This must be done very quickly, as the pole pieces become warm, while also the search coil cools down and at the lower temperature its area is smaller, (and just on this area is based the measurement of the field). Particularly the latter must be avoided as the coefficient of expansion of the material (a hard kind of colophonium) was not known. The coil had been compared previously with a carefully polished glass standard coil. [2]) The influence of the temperature on the field proved to be negligible.

The current through the magnet, was read on a precision instrument of SIEMENS and HALSKE. The resistance measurements were carried out at very short intervals. This was desirable to eliminate

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[1]) H. DU BOIS, Ann. der Physik. **42** p. 968, 1913.

[2]) See W. J. DE HAAS and P. DRAPIER, Ann. der Physik. **42**, p. 673, 1913.

the influence of fluctuations in the magnet current. The current was taken from the central Berlin lighting circuit net. The chief errors in the measurements were due to the temperature and to a less extent to the field measurement. An unfavourable circumstance is, that the effect is roughly proportional to the square of the field, so that an error in the field gets a double weight. When an accuracy of $^1/_3\,^0/_0$ is desired, the magnetic field must be known to $^1/_{600}$ and this accuracy is not so easily attained as is often supposed.

The purpose of this research was not to make very accurate measurements, but to see, whether in this case also the orientation of the crystal axis has a great influence. For graphite this has already been proved by D. E. ROBERTS (loc. cit.), for bismuth by VAN EVERDINGEN[1]) and LOWNDS[2]).

§ 2. *Temperature curve without field.* First the change of the resistance of antimony in the basic plane was investigated. The specific resistance was not determined because of the undefiniteness of the soldering places, which much diminishes the accuracy of the measurements. The different temperatures were reached on the principle of the HENNING[3]) cryostate. In a vacuum vessel with petroleum ether was put a tube, which was closed at the lower end. With a vacuum siphon this tube was filled with liquid air. This filling was not regulated automatically, but with the hand. The temperature was read on a pentane thermometer.

After some practice it was found that by good stirring the temperature could be kept sufficiently constant. Below — 140° the petroleum ether became thick, which made good stirring difficult and for this reason the lowest points were measured in the liquid air itself. At — 190° the curve $R/R_0 = (\theta)$ (fig. 1) does not yet show a point of inflexion. The greater the purity of the bismuth the lower the temperature at which the point of inflexion occurs and the weaker this point of inflexion. From this we may also conclude, that the antimony from MERCK was very pure[4]). From the observed values a formula $R = R_0\,(1 + \alpha\theta + \beta\theta)$ was calculated by the method of least squares.

Such a formula holds within this range of temperature. The formulae of NERNST, KAMERLINGH ONNES and WIEN have not been

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[1]) E. VAN EVERDINGEN, Comm. Leiden N⁰. 26. 37. 40. 41. 42. 48. 53. 58. 61. 63. 72. Suppl. 2.

[2]) L. LOWNDS, Ann. der Phys. **6** p. 146, 1901; **9** p. 677, 1902.

[3]) F. HENNING, Zeitschr. f. Instrk. **33** p. 33, p. 1913.

[4]) F. C. BLAKE, loc. cit. Table I.

tried, partly because they do not refer to these low temperatures, partly because we have not, as far as they have been derived from the quantum theory, enough data, at least not for crystalline antimony.

Fig. 1 shows the curve R/R_0; except at — 32.9° it coincides very well with the experimental curve.

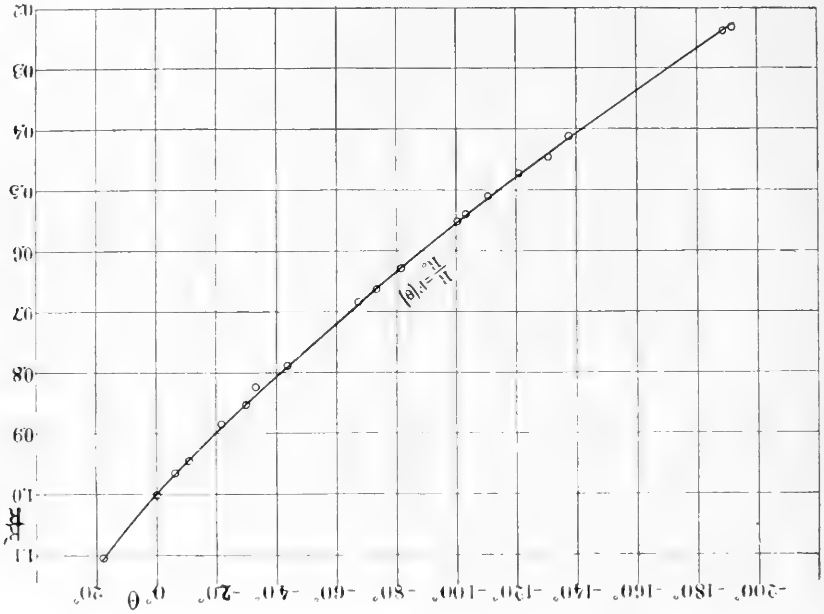

Fig. 1.

The values have been collected in table 1. The differences between the observed values and those calculated from the above mentioned formula with two coefficients are about $1^0/_0$; it would be possible to get better agreement with a formula containing more coefficients but this was of no value since on account of the indefiniteness of the soldered joints an accuracy of $1\,^0/_0$ is as much as can be expected.

The values in table I have been calculated with the formula:

$$R = R_0\,(1 + 0{,}005111\,\theta + 0{,}000005654\,\theta^2)\,. \quad . \quad . \quad . \qquad (1)$$

The linear coefficient of expansion is therefore somewhat greater in the basic plane than in other directions.

The "Recueil de Constantes Physiques" gives α 0,0039 [1]. This agrees with the measurements of EUCKEN and GEHLHOFF [2]), who find for the electric conductivity of a cast stick of antimony at

0°	— 79°	— 190°
$2{,}565.10^4$	$3{,}568.10^4$	$9{,}56.10^4$

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[1] Recueil de Const. Phys. p. 584, 1913.

[2] A. EUCKEN und G. GEHLHOFF, Verh. d. D. Phys. Gesellsch. **14**, p. 169, 1912.

TABLE 1.

θ C.	R/R_0 Observation	R/R_0 Calculation	$O-C$	%
18°	1.104	1.094	+ 0.01	+ 1%
0	1.000	1.000		
— 6.1	.962	.971	— .01	— 1
— 10.8	.942	.951	— .009	— 1
— 21.5	.883	.892^5	— .009	— 1
— 29.9	.851	.850	+ .001	+ $^1/_8$
— 32.9	.822	.839	— .017	— 2
— 43.5	.787	.788	— .001	— $^1/_8$
— 67	.684	.683	+ .001	+ $^1/_7$
— 73	.663	.657	+ .006	+ $^1/_7$
— 81	.626	.623	+ .003	+ $^1/_2$
— 98.9	.545	.551	— .006	— 1
— 102.6	.537	.535	+ .002	+ $^1/_2$
— 110	.507	.506	+ .001	+ $^1/_5$
— 120.2	.470	.468	+ .002	+ $^1/_2$
— 120.9	.473	.465	+ .008	+ 2
— 130	.443	.432	+ .011	+ 2
— 137	.408	.406	+ .002	+ $^1/_2$
— 188	.235	.240	— .005	— 2
— 191	.228	.230	— .002	— 1

and with earlier experiments of von Bose and Matthiesen[1]) who found for the conductivity between 10° and 100°:

$$\lambda = 4,6172 - 0,018389\,\theta + 0,00004785\,\theta^2$$

§ 3. *Orientation curve.*

This was determined at 18° and about 23 K.G. The resistance of the crystal was measured with the axis normal and parellel to the

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[1]) v. Bose und Mathiessen, Pogg. Ann. **115**, p. 353, 1862.

field and in different positions between these two principal ones. The current for the measurements was always normal to the field, the direction of which is shown by the arrow in fig. 2. It was found (see fig. 2) that in the maximum and minimum positions, which were normal to each other, the values $\frac{R'-R}{R}$ did not differ much, much less than in the cases of graphite and bismuth. For these conductors in one of these principal positions I the effect is so much smaller than in the other one II, that Roberts [1]) thought it possible, that in position I there does not exist an effect at all. The small observed effect might be caused by an imperfect orientation in the field. In this case a small component of the effect belonging to position II would be observed. For antimony the differences between the results in the positions I and II are so small, that this explanation seems not to hold. It is therefore probable, that metal crystals show for a definite direction of the current, normal both to the principal axis and to the field, two independent magnetic resistance changes, the one when the principal axis has the direction of the field, the other when it is normal to it. Other cases for intermediate positions can be reduced to these. The above observations, that for bismuth and graphite, i.e. for those crystals which show the greatest resistance change in the field, the difference between the resistance curves in the two principal positions is greatest, agree with a remark of C. W. Heaps [2]). Heaps, who worked with conglomerates, points out

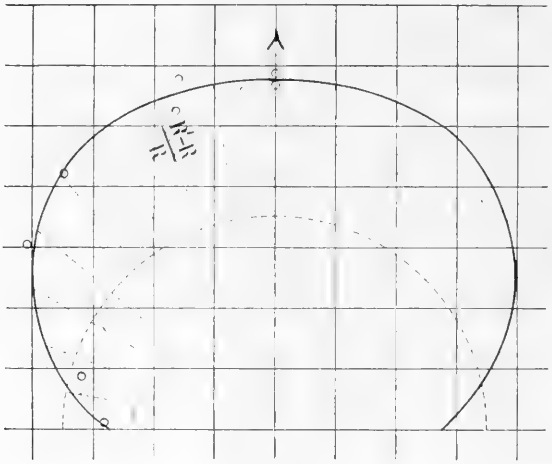

Fig. 2.

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[1]) D. E. Roberts, loc. cit. p. 469.

[2]) C. W. Heaps Phil. Mag, VI **24** p. 815. 1912.

that those metals, which show the greatest resistance change also give the most different resistance curves in a tranverse and a longitudinal field. I hope to return to this point later. Fig 2 shows the orientation curve.

The full line represents the formula:

$$\left.\begin{aligned}\frac{R'_{18}-R_{18}}{R_{18}} &= [0{,}519-0{,}510\ sin\ 1{,}125\ (81-|\mathfrak{H}\ sin\ \varphi|)] \\ &+ [0{,}167-0{,}1696\ sin\ 2{,}665\ (30-|\mathfrak{H}\ cos\ \varphi|)]\end{aligned}\right\}^{1)} \quad . \quad . \quad (2)$$

where φ is the angle between the direction of the field and the principal axis of the crystal.

To represent the resistance change in the field in one of the two principal directions, different types of formulae were tried. Finally certain considerations, which may be omitted here, led to the form $\frac{R'}{R} = a + b\ sin\ c\ (d - |\mathfrak{H}|)$ (3). Because of the connexion between the constants for the field $\mathfrak{H} = 0$, this formula has three constants. The above formula (2) is derived from (3) by resolving the $\mathfrak{H}$ under the sin. into its components. As $R' - R$ is very small compared with R and as there were no special precautions taken with regard to the orientation, we may regard the agreement of the observed points ⊙ with the calculated ones as fairly satisfying.

§ 4. *Isothermal curves.* Fig 3.

As to these we may remark, that the quasi-linear part of the field curves is already reached at 30 KG. Of earlier investigations must be mentioned those of LENARD [2]), who used pressed antimony wire, 0.2 mm. thick. This highest field was 6.6 KG. where he found $\frac{R'}{R} = 1.012$ for a constant current; and also those of v. ETTINGSHAUSEN [3]), LEBRET [4]) and BARLOW [5]).

Fig. 3 shows the field curves for 18° and —188° in two principal directions. The formulae used are:

Table 2. $\frac{R'_{18^0}}{R_{18^0}} = 1.519 - 0.510\ \ sin\ 1.125\ (81 - |\mathfrak{H}_{//}|)$

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[1]) In this and in the other formula φ is expressed in degrees.

[2]) PH. LENARD, Wied. Ann. **39**, p. 637, 1890.

[3]) A. v. ETTINGSHAUSEN, Wien. Akad. Ber. **59**, p. 714, 1887.

[4]) A. LEBRET, Diss. Leiden, 1895.

[5]) G. BARLOW, Ann. d. Phys., **12**, p. 916, 1903.

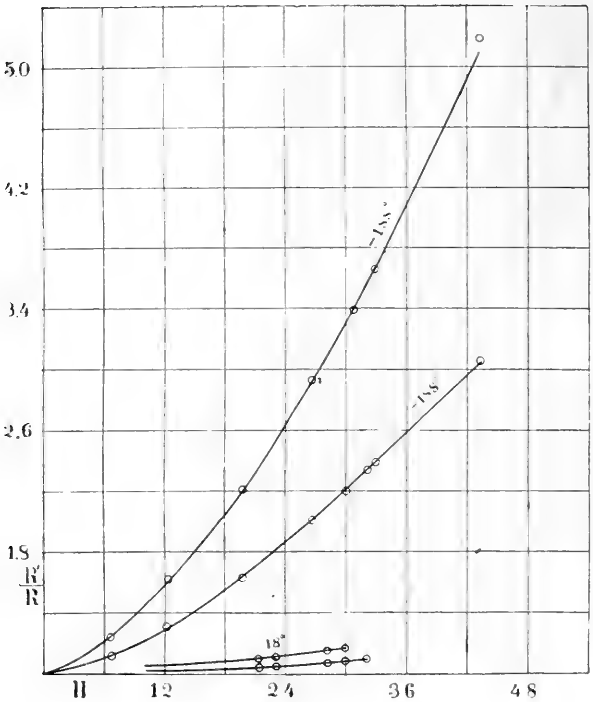

Fig. 3.

Table 3. $= 1.167 - 0.1696\, sin\, 2.665\, (30 - |\mathfrak{H}_{\perp}|)$

„ 4. $\frac{R'_{-188^0}}{R_{-188^0}} = 2.742 - 1.80\, sin\, 2.022\, (38.55 - |\mathfrak{H}_{//}|)$

„ 5. $= 10.08 - 0.965\, sin\, 1.069\, (74.90 - |\mathfrak{H}_{\perp}|)$.

TABLE 2.

Antim. resist. as a funct.
of θ and .
axis // field.

$\mathfrak{H}$ Kilogauss	$\theta = 18°$	
	$\frac{R'}{R}$ (O)	$\frac{R'}{R}$ (C)
21.4	1.039	1.038
23.2	1.047	1.048
28.3	1.071^4	1.072^5
29.98	1.079	1.082
32.0	1.091	1.092

TABLE 3.

Antim. resist. as a funct.
of θ and $\mathfrak{H}$.
axis ⊥ field.

$\mathfrak{H}$ Kilogauss	$\theta = 18°$	
	$\frac{R'}{R}$ (O)	$\frac{R'}{R}$ (C)
21.4	1.101	1.101^5
23.2	1.114	1.114
28.3	1.154	1.155
29.98	1.167	1.167

The observed points have again been marked ⊙. In tabel 2, 3, 4, and 5 the numbers are given.

TABLE 4.
Antim. resist. as a funct. of θ and $\mathfrak{H}$.
axis // field.

$\mathfrak{H}$ Kilogauss	$\theta = -188°$	
	$\frac{R'}{R}(O)$	$\frac{R'}{R}(C)$
6.7	1.121	1.117
12.2	1.310	1.297
19.8	1.630	1.633
26.7	2.013	2.010
30.1	2.200	2.212
32.2	2.340	2.343
33.0	2.392	2.392
43.3	3.060	3.045

TABLE 5.
Antim. resist. as a funct. of θ and $\mathfrak{H}$.
axis ⊥ field.

$\mathfrak{H}$ Kilogauss	$\theta = -188°$	
	$\frac{R'}{R}(O)$	$\frac{R'}{R}(C)$
6.6	1.239	1.238
12.4	1.620	1.607
19.8	2.210	2.192
26.7	2.937	2.920
30.9	3.396	3.401
33.0	3.664	3.666
43.3	5.195	5.105

In order to test formula (3) still further it has been applied to the observations of KAMERLINGH ONNES and BECKMAN.

The tables 6, 7, 8, 9 have been taken from Comm. N°. 129 and 130 Phys. Lab. Leiden. In the columns $\frac{R'}{R_0}(O)$ are given the observed values, while under $\frac{R'}{R_0}(C)$ are to be found the values calculated from the formula at the head of the table.

$$T = 15°. \quad \frac{R'}{R_0} = 68.4 - 68.76 \, sin \, 5.45 \, (15.05 - |\mathfrak{H}|)$$

$$T = 20.3°. \quad \frac{R'}{R_0} = 75.74 - 76.1 \, sin \, 5.09 \, (16.3 - |\mathfrak{H}|)$$

$$T = 72°. \quad \frac{R'}{R_0} = 134\ 057 - 133.9 \, sin \, 2.166 \, (40 - |\mathfrak{H}|)$$

$$T = 90°. \quad \frac{R'}{R_0} = 102.34 - 102\ 15 \, sin \, 2.04 \, (42.15 - |\mathfrak{H}|)$$

TABEL 6.

Resistance of Bi_{dl} as a function of temperature and field.

$\mathfrak{H}$ Gauss	$T = 15°$ K.			$T = 20.3°$ K.		
	R'	$\frac{R'}{R_0(O)}$	$\frac{R'}{R_0(C)}$	R'	$\frac{R'}{R_0(O)}$	$\frac{R'}{R_0(C)}$
0	0.526	0.216	0.25	0.588	0.242	0.24
2760				11.5	4.73	4.74
3850	19.9	8.185	8.32			
5540	34.9	14.35	14.38	32.8	13.50	13.69
7370	55.9	23.00	22.48	54.7	22.50	21.44
9200	80.8	33.25	32.14	76.7	31.55	30.86
11850	116.4	47.90	47.82	113.2	46.55	46.47
13600	143.1	58.85	58.95	141.5	58.20	57.69
15670	175.6	72.25	72.45	172.	70.75	71.48
17080	199.3	82.00	81.18	196.5	80.85	81.00

TABLE 7.

Resistance of Bi_{dl} as a function of temperature and field.

$\mathfrak{H}$ Gauss	$T = 72°$ K.			$T = 90°$ K.		
	R'	$\frac{R'}{R_0(O)}$	$\frac{R'}{R_0(C)}$	R'	$\frac{R'}{R_0(O)}$	$\frac{R'}{R_0(C)}$
0	0.989	0.407	0.407	1.075	0.442	0.490
2760	4.68	1.926	1.919	3.92	1.613	1.54
5540	12.28	5.052	4.957	9.24	3.80	3.86
7370	19.10	7.86	7.66	14.20	5.84	5.82
9200	26.6	10.94	11.01	19.74	8.12	8.14
11850	41.2	16.95	16.92	29.82	12.27	12.34
13600	52.4	21.6	21.5	38.60	15.88	15.52
15670	67.2	27.65	27.57	48.05	19.77	19.68
17080	77.8	32.0	32.03	55.80	22.96	22.79

$$T = 170^\circ. \qquad \frac{R'}{R_0} = 10.47 - 10.08 \sin 2.46\,(31.36 - |\mathfrak{H}|)$$

$$T = 290^\circ. \qquad \frac{R'}{R_0} = 1.657 - 0.749 \sin 4.5\,(12 - |\mathfrak{H}|)$$

TABLE 8.

Resistance of Bi_{dl} as a function of temperature and field.

$\mathfrak{H}$ Gauss	$T = 170^\circ$ K.			$T = 290^\circ$ K.		
	R'	$\frac{R'}{R_0(O)}$	$\frac{R'}{R_0(C)}$	R'	$\frac{R'}{R_0(O)}$	$\frac{R'}{R_0(C)}$
0	1.570	0.646	0.630	2.570	1.057	1.051
2760	2.366	0.973	0.98	2.770	1.140	1.162
5540	3.657	1.504	1.47	3.110	1.280	1.294
7370	4.612	1.897	1.83	3.473	1.388	1.392
9200	5.613	2.310	2.25	3.635	1.495	1.494
11850	7.299	3.003	3.00	4.002	1.646	1.654
13600	8.506	3.500	3.51	4.248	1.746	1.750
15670	10.204	4.199	4.19	4.540	1.868	1.869
17080	11.412	4.695	4.69			

§ 5. *General remarks and conclusions.* Referring to the existing observations we may make some remarks on the electron theory of metals.

The sign of the HALL-effect shows, that the influence of the magnetic field on the so-called "free" electrons is a complicated phenomenon. The change of the resistance in the magnetic field can give us an insight into the mechanism of the electric current. For it has been found, that the resistance change of a crystal depended only on the angle between the crystal axis and the field [1]); the angle between the directions of the field and of the current is of no importance, at least in a first approximation. From this we may conclude, that although the electrons may be "free" in passing from one molecule to the other, the influence of the field on these free paths and the resistance change caused by it, is negligible. Therefore theories as e.g. that of J. J. THOMSON, which try to calculate the phenomenon from the direct effect of the field on the "free" electrons cannot possibly give the right result.

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[1]) D. E. ROBERTS, loc. cit. p. 468. Table II.

The field produces the change of resistance through its effect on the molecules and not on the "free" electrons (when these indeed exist) and it is natural to suppose that the field has also an orientating influence on diamagnetic molecules. From the magnetic double refraction COTTON and MOUTON have also concluded, that for diamagnetic substances too the field has a directing influence [1]). One can readily imagine, that anisotropic molecules have, in general, a greater magnetic moment than isotropic molecules; therefore, if the magnetic moment is already present before the field is excited, the field will have a stronger directing influence on anisotropic molecules. Similarly if we suppose, as is generally done, that diamagnetism is an induced phenomenon, we may assume that a bigger moment is produced in an anisotropic molecule than in an isotropic one. We may therefore conclude that the crystal system must have an influence on the phenomenon.

Now we find this to be really the case. All substances, which show a large or rather large resistance change, belong to the hexagonal system, while those which have a much smaller effect belong to the regular system.

Finally we may still remark, that those molecules, which have a large susceptibility and which are besides anisotropic will undergo the greatest influence of the magnetic field. And as the resistance change is caused by a directing effect, there must be a connection between susceptibility and resistance change. That this connection really exists is proved by the experiments. It is from this connexion that a large effect for graphite could be predicted [2]).

When we put the diamagnetic metals in a series in the order of the values of $(R'—R)/R$, beginning with the largest value, we have first:

Bismuth.
Graphite.
Antimony.
Then according to:

GRUNMACH	PATTERSON	HEAPS
Cadmium	Cadmium	Tellurium
Zinc	Zinc	Cadmium
Silver		Zinc
Gold	Gold	Gold
Copper	Copper	
Lead		

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[1]) A. COTTON and H. MOUTON, Journal de Physique (5) **1** p. 40, 1911. P. LANGEVIN, le Radium **7** p. 249, 1910.

[2]) D. E. ROBERTS, loc. cit.

The definite series is: Bismuth Graphite Antimony Tellurium Cadmium Zinc Silver Gold Copper Lead.

Hexagonal are:	and regular:
Bismuth	Silver
Graphite	Gold
Antimony	Copper
Tellurium	Lead
Cadmium	
Zinc	

The order of the diamagnetic susceptibilities is according to MORRIS OWEN[1]:

	χ	
Bismuth	-1.40×10^{-6}	Hexagonal
Graphite[2]	-5	
Antimony	-0.815	
Tellurium	-0.303	
Cadmium	-0.185	
Zinc	-0.151	
Silver	-0.201	Regular
Gold	-0.152	
Lead	-0.120	
Copper	-0.085	

The division into two crystallographic groups and a remarkable regularity in each of these groups are obvious.

CONCLUSION.

1. For all temperatures the resistance change of diamagnetic substances in the magnetic field can be represented by a formula of the form $R'/R = a - b \sin c\,(d + |\mathfrak{H}|)$.

2. The field has a directing influence on the diamagnetic metal molecules.

3. There exists a connexion between crystal system, resistance change and diamagnetic susceptibility.

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[1] M. OWEN. Ann. d. Phys. **37**, p. 657, 1912.

[2] As to the place of graphite one must take into account that different kinds of graphite differ greatly in properties. Further, no account is taken of the influence of temperature on the order in the series. All series are given for room temperature. It seems probable that in grouping at "corresponding" temperatures and "corresponding" states lead would also change its place.

Mathematics. — *"The theory of* BRAVAIS *(on errors in space) for polydimensional space, with applications to Correlation."* By Prof. M. J. VAN UVEN. (Communicated by Prof. J. C. KAPTEYN).

(Communicated in the meeting of March 28, 1914).

In the original treatise of BRAVAIS: "Analyse mathématique sur les probabilités des erreurs de situation d'un point"[1]) as well as in the articles that have afterwards appeared on this subject[2]) the problem of the distribution of errors in space has only been investigated for spaces of two and three dimensions. Only Prof. K. PEARSON has also treated the case of four-dimensional space[3]).

It may be interesting to treat this problem also for a space of an arbitrary number of dimensions, not so much with a view to the geometrical side of the problem, as in connection with the subject of correlation. If we consider the problem from this point of view, it comes to this:

A number (σ) of variables $u_1, u_2, \ldots u_\sigma$, are given, each of which follows GAUSS's exponential law:

$$\delta W_i = \frac{h_i}{\sqrt{\pi}} e^{-h_i^2 u_i^2} \delta u_i$$

and consequently may assume any value between $-\infty$ and $+\infty$.

Further we have a certain number (ϱ) of linear functions $x_1, x_2, \ldots x_\varrho$ of the variables u_i, viz.,

$$\begin{aligned} x_1 &= a_{11}u_1 + a_{12}u_2 + \ldots + a_{1\sigma}u_\sigma, \\ x_2 &= a_{21}u_1 + a_{22}u_2 + \ldots + a_{2\sigma}u_\sigma, \\ &\vdots \\ x_\varrho &= a_{\varrho 1}u_1 + a_{\varrho 2}u_2 + \ldots + a_{\varrho\sigma}u_\sigma. \end{aligned}$$

The probability that x_j ranges between ξ_j and $\xi_j + \delta\xi_j$ ($j = 1, 2, \ldots \varrho$) is then expressed by the formula

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[1]) A. BRAVAIS. "Anal. math. etc." Paris: Mémoires présentés par divers savants à l'Académie royale des sciences de l'Institut de France; T. 9 (1846), p. 255.

[2]) E. CZUBER. Theorie der Beobachtungsfehler. Leipzig, 1891, Teubner; p. 350.
M. D'OCAGNE. Sur la composition des lois d'erreurs de situation d'un point; Comptes Rendus T. 118 (1894), p. 512; Bulletin de la Soc. math. de France, T. 23 (1895), p. 65; Annales de la Soc. scientif. de Bruxelles, T. 18 (1894) p. 86.
S. H. BURBURY. On the Law of Error in the case of correlated variations; Report of the British Assoc. (65th m.) (1895), p. 621.
V. REINA. Sulla probabilità degli errori di situazioni di un punto nello spazio; Atti della R. Accad. dei Lincei, serie 5a, T. 6, sem. 1 (1897), p. 107.

[3]) K. PEARSON. Mathematical contributions to the Theory of Evolution: Regression; Phil. Trans. vol. 187 (1895), p. 253.

$$W = \sqrt{\frac{E}{\pi^{\rho}}} \,.\, e^{-H} \delta\xi_1, \delta\xi_2 \ldots . \delta\xi_{\rho},$$

in which

$$H = b_{11}\xi_1^2 + 2b_{12}\xi_1\xi_2 + \ldots . + b_{\rho\rho}\xi_{\rho}^2.$$

The aim of this paper is:

1. to express the coefficients b_{jk} of the quadratic expression H and the quantity E in the coefficients a_{ji},

2. to elucidate the notion of a *coefficient of correlation* by means of the expressions found.

The probability of the simultaneous occurrence of the values $u_1, u_2, \ldots u_{\sigma}$ is

$$\delta W = \frac{\prod\limits_1^{\sigma} h_i}{\pi^{\frac{\rho}{2}}} e^{-\sum\limits_1^{\sigma} h_i^2 u_i^2} \prod_1^{\sigma} \delta u_i .$$

We begin by writing

$$h_i u_i = v_i \qquad (i = 1,2, \ldots \sigma)$$

and

$$\alpha_{ji} = h_i a_{ji} \qquad (j = 1,2, \ldots \varrho ; \;\; i = 1,2, \ldots \sigma).$$

Thus we get

$$\delta W = \frac{1}{\pi^{\frac{\sigma}{2}}} e^{-\sum\limits_1^{\sigma} v_i^2} \prod_1^{\sigma} \delta v_i$$

and

$$\begin{aligned} x_1 &= \alpha_{11} v_1 + \alpha_{12} v_2 + \ldots + \alpha_{1\sigma} v_{\sigma}, \\ x_2 &= \alpha_{21} v_1 + \alpha_{22} v_2 + \ldots + \alpha_{2\sigma} v_{\sigma}, \\ &\vdots \\ x_{\rho} &= \alpha_{\rho 1} v_1 + \alpha_{\rho 2} v_2 + \ldots + \alpha_{\rho\sigma} v_{\sigma}. \end{aligned}$$

For the present we shall continue working with the coefficients a_{ji} only in the final result.

Like Bravais we moreover introduce $\sigma - \varrho$ auxiliary variables, viz,

$$\begin{aligned} x_{\rho+1} &= \sum_1^{\sigma} \alpha_{\rho+1,i}\, v_i \\ &\vdots \\ x_{\sigma} &= \sum_1^{\sigma} \alpha_{\sigma i}\, v_i \end{aligned}$$

The determinant of substitution of $\begin{pmatrix} x_1, x_2, \ldots x_{\sigma} \\ v_1, v_2, \ldots v_{\sigma} \end{pmatrix}$ is then

$$\Delta = \begin{vmatrix} a_{11}, a_{12}, \ldots a_{1\sigma} \\ a_{21}, a_{22}, \ldots a_{2\sigma} \\ \vdots \quad \vdots \qquad \vdots \\ a_{\sigma 1}, a_{\sigma 2}, \ldots a_{\sigma\sigma} \end{vmatrix} = |a_{ji}|.$$

The algebraic complement of a_{ji} we call A_{ji}.

By the substitution $\begin{pmatrix} x \\ v \end{pmatrix}$

$$H = \sum_1^\sigma v_i^2$$

becomes

$$H = \sum_1^\sigma b_{jj}\, x_j^2 + 2 \sum_1^\sigma b_{jk}\, x_j\, x_k.$$

The functions $x_1, \ldots x_\rho$ are given. We now dispose of the remaining $(x_{\rho+1}, \ldots x_\sigma)$ in such a manner that the following relations are satisfied:

$$b_{jk} = 0 \quad \text{for} \quad j = 1,2, \ldots \sigma \quad ; \quad k = \rho + 1, \ldots \sigma.$$

In this way we attain that the introduced $\sigma - \rho$ auxiliary variables occur only squared.

Solving v_i from the equations of substitution we find

$$v_i = \frac{\sum\limits_{j=1}^{\sigma} A_{ji}\, x_j}{\Delta} \qquad (i = 1,2 \ldots \sigma).$$

Consequently we find for H

$$H = \sum_1^\sigma v_i^2 = \frac{\sum\limits_{i=1}^{\sigma} \left(\sum\limits_{j=1}^{\sigma} A_{ji}\, x_j \right)^3}{\Delta^2} = \frac{\sum\limits_{i=1}^{\sigma} (A_{1i}\, x_1 + A_{\iota}\;\, x_2 + \ldots + A_{\sigma i}\, x_\sigma)^2}{\Delta^2} =$$

$$= \frac{\sum\limits_{i=1}^{\sigma} (A_{i1}^2\, x_1^2 + 2 A_{1i} A_{2i}\, x_1\, x_2 + \ldots + A_{\sigma i}^2\, x_\sigma^2)}{\Delta^2} =$$

$$= \frac{\sum\limits_{i=1}^{\sigma} A_{1i}^2 \,.\, x_1^2 + 2 \sum\limits_{i=1}^{\sigma} A_{1i} A_{2i} \,.\, x_1\, x_2 + \ldots + \sum\limits_{1}^{\sigma} A_{\sigma i}^2 \,.\, x_\sigma^2}{\Delta^2} =$$

$$= \frac{\sum\limits_{j=1}^{\sigma} \left(\sum\limits_{j=1}^{\sigma} A_{ji}^2 \right) x_j^2 + 2 \sum\limits_{j=1,k=1}^{\sigma} \left(\sum\limits_{i=1}^{\sigma} A_{ji} A_{ki} \right) x_j\, x_k}{\Delta^2},$$

or putting

$$\frac{\sum\limits_{i=1}^{\sigma} A_{ji}^2}{\Delta^2} = b_{jj} \quad ; \quad \frac{\sum\limits_{i=1}^{\sigma} A_{ji} A_{ki}}{\Delta^2} = b_{jk} \; (= b_{kj})$$

$$H = \sum_{j=1}^{\sigma} b_{jj}\, x_j^2 + 2 \sum_{j=1,k=1}^{\sigma} b_{jk}\, x_j\, x_k.$$

We must now try to express the coefficients b_{jj} and b_{jk} for $j = 1, 2, \ldots \varrho$, $k = 1, 2, \ldots \varrho$, in terms of the coefficients of the given equations of substitution:

$$x_1 = \Sigma\, a_{1i} v_i, \ldots, x_\rho = \Sigma\, a_{\rho i} v_i.$$

The conditions $b_{jh} = 0$ for $h = \varrho + 1, \ldots \sigma$ are equivalent with the conditions

$$\sum_{i=1}^{\sigma} A_{ji} A_{hi} = 0 \quad \text{for} \quad h = \varrho + 1, \ldots \sigma;$$

but

$$\sum_{i=1}^{\sigma} A_{ji} a_{ji} = \Delta$$

$$\sum_{i=1}^{\sigma} A_{ji}\, a_{li} = 0 \quad \text{for} \quad l \neq j.$$

are also always satisfied.

So we have the following set of equations,

$$\Sigma A_{ji} a_{1i} = 0,\ \Sigma A_{ji} a_{2i} = 0, \ldots \Sigma\, A_{ji} a_{j-1,i} = 0,\ \Sigma\, A_{ji} a_{ji} = \Delta,$$
$$\Sigma\, A_{ji} a_{j+1,i} = 0, \ldots \Sigma\, A_{ji} a_{\rho i} = 0,\ \Sigma\, A_{ji} A_{ki} = \Delta^2\, b_{jk},$$
$$\Sigma\, A_{ji} A_{\rho+1,i} = 0, \ldots, \Sigma\, A_{ji} A_{\sigma i} = 0.$$

Hence

$$\begin{vmatrix} a_{11} & a_{12} & \ldots a_{1\sigma} & 0 \\ a_{21} & a_{22} & \ldots a_{2\sigma} & 0 \\ \vdots & \vdots & \vdots & \vdots \\ a_{j-1,1} & a_{j-1,2} & \ldots a_{j-1,\sigma} & 0 \\ a_{j1} & a_{j2} & \ldots a_{j\sigma} & \Delta \\ a_{j+1,1} & a_{j+1,2} & \ldots a_{j+1,\sigma} & 0 \\ \vdots & \vdots & \vdots & \\ a_{\rho 1} & a_{\rho 2} & \ldots a_{\rho\sigma} & 0 \\ A_{k1} & A_{k2} & \ldots A_{k\sigma} & \Delta^2 b_{jk} \\ A_{\rho+1,1} & A_{\rho+1,2} & \ldots A_{\rho+1,\sigma} & 0 \\ \vdots & \vdots & \vdots & \\ A_{\sigma 1} & A_{\sigma 2} & \ldots A_{\sigma\sigma} & 0 \end{vmatrix} = 0$$

or

$$\Delta b_{jk} \begin{vmatrix} a_{11} & a_{12} & \ldots a_{1\sigma} \\ a_{21} & a_{22} & \ldots a_{2\sigma} \\ \vdots & \vdots & \vdots \\ a_{\rho 1} & a_{\rho 2} & \ldots a_{\rho\sigma} \\ A_{\rho+1,1} & A_{\rho+1,2} & \ldots A_{\rho+1,\sigma} \\ \vdots & \vdots & \vdots \\ A_{\sigma 1} & A_{\sigma 2} & \ldots A_{\sigma\sigma} \end{vmatrix} = (-1)^{\rho+j} \begin{vmatrix} a_{11} & a_{12} & \ldots\ a_{1\sigma} \\ a_{21} & a_{22} & \ldots\ a_{2\sigma} \\ \vdots & \vdots & \vdots \\ a_{j-1,1} & a_{j-1,2} & \ldots\ a_{j-1,\sigma} \\ a_{j+1,1} & a_{j+1,2} & \ldots\ a_{j+1,\sigma} \\ \vdots & \vdots & \vdots \\ a_{\rho 1} & a_{\rho 2} & \ldots\ a_{\rho\sigma} \\ A_{k1} & A_{k2} & \ldots A_{k\sigma} \\ A_{\rho+1,1} & A_{\rho+1,2} & \ldots A_{\rho+1,\sigma} \\ \vdots & \vdots & \vdots \\ A_{\sigma 1} & A_{\sigma 2} & \ldots A_{\sigma\sigma} \end{vmatrix}$$

or

$$\Delta b_{jk}\;.\;N=(-1)^{\rho+j}\,T_{jk}.$$

Now the following relation holds good:

$$N=\Sigma\begin{vmatrix} a_{1r_1}, & a_{1r_2}, \ldots & a_{1r_\rho} \\ a_{2r_1}, & a_{2r_2}, \ldots & a_{2r_\rho} \\ \vdots & \vdots & \vdots \\ a_{\rho r_1}, & a_{\rho r_2}, \ldots & a_{\rho r_\rho} \end{vmatrix}\times\begin{vmatrix} A_{\rho+1,\,r_{\rho+1}}, & A_{\rho+1,\,r_{\rho+2}}, \ldots & A_{\rho+1,\,r_\sigma} \\ A_{\rho+2,\,r_{\rho+1}}, & A_{\rho+2,\,r_{\rho+2}}, \ldots & A_{\rho+2,\,r_\sigma} \\ \vdots & \vdots & \vdots \\ A_{\sigma r_{\rho+1}}, & A_{\sigma r_{\rho+2}}, \ldots & A_{\sigma r_\sigma} \end{vmatrix}.$$

in which $r_1, r_2, \ldots r_\rho, r_{\rho+1}, \ldots r_\sigma$ represents a permutation of numbers $1, 2, \ldots \sigma$ and the summation must be extended over all these permutations.

As

$$\begin{vmatrix} A_{\rho+1,\,r_{\rho+1}}, & \ldots & A_{\rho+1,\,r_\sigma} \\ \vdots & & \vdots \\ A_{\sigma r_{\rho+1}} & , \ldots & A_{\sigma r_\sigma} \end{vmatrix}$$

is the minor of the reciprocal determinant

$$\overline{\Delta}=\begin{vmatrix} A_{11}, & A_{12}, \ldots & A_{1\sigma} \\ A_{21}, & A_{22}, \ldots & A_{2\sigma} \\ \vdots & \vdots & \vdots \\ A_{\sigma 1}, & A_{\sigma 2}, \ldots & A_{\sigma\sigma} \end{vmatrix}$$

which corresponds to the algebraic complement of

$$\begin{vmatrix} a_{1r_1}, & \ldots & a_{1r_\rho} \\ \vdots & & \vdots \\ a_{\rho r_1}, & \ldots & a_{\rho r_\rho} \end{vmatrix},$$

we have the relation

$$\begin{vmatrix} A_{\rho+1,\,r_{\rho+1}}, & \ldots & A_{\rho+1,r_\sigma} \\ \vdots & & \vdots \\ A_{\sigma r_{\rho+1}} & , \ldots & A_{\sigma r_\sigma} \end{vmatrix}=\Delta^{\sigma-\rho-1}\begin{vmatrix} a_{1r_1}, & \ldots & a_{1r_\rho} \\ \vdots & & \vdots \\ a_{\rho r_1}, & \ldots & a_{\rho r_\rho} \end{vmatrix}.$$

Consequently we find for N

$$N=\Delta^{\sigma-\rho-1}\times\Sigma\begin{vmatrix} a_{1r_1}, & \ldots & a_{1r_\rho} \\ \vdots & & \vdots \\ a_{\rho r_1}, & \ldots & a_{\rho r_\rho} \end{vmatrix}^2;$$

i.e. N is $\Delta^{\sigma-\rho-1}$ times the sum of the squares of all determinants of the ϱ^{th} order of the matrix

$$M=\begin{vmatrix} a_{11}, & a_{12}, & \ldots & a_{1\sigma} \\ \vdots & & & \vdots \\ a_{\rho 1}, & a_{\rho 2}, & \ldots & a_{\rho\sigma} \end{vmatrix},$$

which is formed from the coefficients of the given equations of substitution.

If we represent such a determinant of the ϱ^{th} order in general by D, we can write

$$N=\Delta^{\sigma-\rho-1}\,\Sigma D^2$$

The numerator T_{jk} is reduced as follows:

$$T_{jk} = \Sigma \begin{vmatrix} a_{1r_1} & , \ldots a_{1r_{\rho-1}} \\ \vdots & \\ a_{j-1,r_1}, & \ldots a_{j-1,r_{\rho-1}} \\ a_{j+1,r_1}, & \ldots a_{j+1,r_{\rho-1}} \\ \vdots & \vdots \\ a_{\rho r_1} & , \ldots a_{\rho r_{\rho-1}} \end{vmatrix} \times \begin{vmatrix} A_{kr_\rho}, & A_{kr_{\rho+1}}, & \ldots\ldots A_{kr_\sigma} \\ A_{\rho+1,r_\rho}, & A_{\rho+1,r_{\rho+1}}, & \ldots A_{\rho+1,r_\sigma} \\ \vdots & \vdots & \vdots \\ A_{\sigma r_\rho}, & A_{\sigma r_{\rho+1}}, & \ldots\ldots A_{\sigma r_\sigma} \end{vmatrix}$$

The determinant

$$D_j = \begin{vmatrix} a_{1i} \\ \vdots \\ a_{j-1,i} \\ a_{j+1,i} \\ \vdots \\ a_{\rho i} \end{vmatrix} \quad (i = r_1, r_2, \ldots r_{\rho-1})$$

belongs to the matrix

$$M_j = \begin{vmatrix} a_{11} & , \ldots a_{1\sigma} \\ \vdots & \vdots \\ a_{j-1,1}, & \ldots a_{j-1,\sigma} \\ a_{j+1,1}, & \ldots a_{j+1,\sigma} \\ \vdots & \vdots \\ a_{\rho 1} & , \ldots a_{\rho\sigma} \end{vmatrix},$$

which is obtained by omitting the row a_{ji} $(i = 1, 2, \ldots \sigma)$ in the matrix M.

Besides

$$\begin{vmatrix} A_{kr_\rho} & , \ldots A_{kr_\sigma} \\ A_{\rho+1,r_\rho}, & \ldots A_{\rho+1,r_\sigma} \\ \vdots & \vdots \\ A_{\sigma r_\rho} & , \ldots A_{\sigma r_\sigma} \end{vmatrix}$$

is the minor of the reciprocal determinant $\overline{\Delta}$, which, apart from the sign, corresponds to the algebraic complement of

$$D_k = \begin{vmatrix} a_{1i} \\ \vdots \\ a_{k-1,i} \\ a_{k+1,i} \\ \vdots \\ a_{\rho i} \end{vmatrix} \quad (i = r_1, r_2 \ \ldots r_{\rho-1})$$

Observing the sign, we have

$$\begin{vmatrix} A_{kr_\rho} & , \ldots A_{kr_\sigma} \\ A_{\rho+1,r_\rho}, & \ldots A_{\rho+1,r_\sigma} \\ \vdots & \vdots \\ A_{\sigma r_\rho} & , \ldots A_{\sigma r_\rho} \end{vmatrix} = (-1)^{\rho+k} \Delta^{\rho-k} . D_k,$$

in which D_k is obtained by omitting the row a_{ki} in the matrix M. So we find

$$T_{jk} = (-1)^{\rho+k} \Delta^{\sigma-\rho} \Sigma D_j D_k,$$

in which the summation must be extended over all determinants of the $(\varrho-1)^{\text{th}}$ order, resp. of the matrices M_j and M_k, and this in such a way that the determinants D_j and D_k in the products are built up from *the same* columns of M.

The coefficients b_{jk} $(j=1, 2, \dots \varrho;\ k=1, 2, \dots \varrho)$ are finally found from

$$\Delta b_{jk} \,.\, \Delta^{\sigma-\rho-1}\, \Sigma D^2 = (-1)^{\rho+j} (-1)^{\rho+k} \Delta^{\sigma-\rho} \Sigma D_j D_k,$$

so that

$$b_{jk} = (-1)^{j+k} \frac{\Sigma D_j D_k}{\Sigma D^2} \quad \left(\begin{matrix} j \\ k \end{matrix} \Big| = 1, 2, \ .\ .\ \varrho\right),$$

and in particular

$$b_{jj} = \frac{\Sigma D_j^2}{\Sigma D^2} \,. \quad (j = 1, 2, \dots \varrho)$$

The determinant of the coefficients b_{jk} $(j, k = 1, 2, \dots \sigma)$ runs

$$| b_{jk} | = \begin{vmatrix} b_{11}, & b_{12}, \dots b_{1\rho}, & 0 & , & 0 & , \dots 0 \\ b_{21}, & b_{22}, \dots b_{2\rho}, & 0 & , & 0 & , \dots 0 \\ \vdots & \vdots \qquad \vdots & \vdots & & \vdots & \vdots \\ b_{\rho 1}, & b_{\rho 2}, \dots b_{\rho\rho}, & 0 & , & 0 & , \dots 0 \\ 0 \ , & 0 \ , \dots 0 \ , & b_{\rho+1, \rho+1}, & & 0 & , \dots 0 \\ 0 \ , & 0 \ , \dots 0 \ , & 0 & , & b_{\rho+2, \rho+2}, & \dots 0 \\ \vdots & \vdots \qquad \vdots & \vdots & & \vdots & \vdots \\ 0 \ , & 0 \ , \dots\ 0 \ , & 0 & , & 0 & , \dots b_{\sigma\sigma} \end{vmatrix},$$

or, if we write

$$\begin{vmatrix} b_{11}, & b_{12}, \dots b_{1\rho} \\ b_{21}, & b_{22}, \dots b_{2\rho} \\ \vdots & \vdots \qquad \vdots \\ b_{\rho 1}, & b_{\rho 2}, \dots b_{\rho\rho} \end{vmatrix} = E$$

$$| b_{jk} | = E \times \prod_{h=\rho+1}^{\sigma} b_{hh};$$

E is the determinant of the quadratic expression H in $x_1, x_2, \dots x_\rho$

As the determinant quadratic expression in $v_1, v_2, \dots v_\sigma$ has the value 1, we have

$$| b_{jk} | = \frac{1}{\Delta^2},$$

hence

$$\Delta = \frac{1}{\sqrt{E \,.\, \prod\limits_{\rho+1}^{\sigma} b_{hh}}}\,.$$

Further we have

$$\prod_{1}^{\sigma} dx_j = \Delta \prod_{1}^{\sigma} dv_i\,,$$

therefore

$$dW = \frac{1}{\pi^{\frac{\sigma}{2}}} e^{-\sum\limits_{1}^{\sigma} v_i^2} \prod_{1}^{\sigma} dv_i = \frac{1}{\pi^{\frac{\sigma}{2}}} \,.\, \frac{e^{-\left(\sum\limits_{1}^{\rho} b_{jj} x_j^2 + 2 \sum\limits_{1}^{\rho} b_{jk} x_j x_k\right)} \times e^{-\sum\limits_{\rho+1}^{\sigma} b_{hh} x_h^2}}{\Delta} \prod_{1}^{\sigma} dx_j =$$

$$= \sqrt{\frac{E}{\pi^{\rho}}} \,.\, e^{-\left(\sum\limits_{1}^{\rho} b_{jj} x_j^2 + 2 \sum\limits_{1}^{\rho} b_{jk} x_j x_k\right)} \,.\, \prod_{1}^{\rho} dx_j \times \sqrt{\frac{\prod\limits_{\rho+1}^{\sigma} b_{hh}}{\pi^{\sigma-\rho}}} \,.\, e^{-\sum\limits_{\rho+1}^{\sigma} b_{hh} x_h^2} \prod_{\rho+1}^{\sigma} dx_h\,.$$

In order to obtain the total probability W we must integrate over $x_{\rho+1}, \ldots x_{\sigma}$ from $-\infty$ to $+\infty$, and over $x_1, x_2, \ldots x_{\rho}$ resp. from $\xi_1, \xi_2, \ldots \xi_{\rho}$ to $\xi_1 + d\xi_1, \xi_2 + d\xi_2, \ldots \xi_{\rho} + d\xi_{\rho}$; i. e. the integration over $x_1, x_2, \ldots x_{\rho}$ consists in this, that in the integrant $x_1, x_2, \ldots x_{\rho}$ are replaced by $\xi_1, \xi_2, \ldots \xi_{\rho}$, while $dx_1, dx_2, \ldots dx_{\rho}$ are resp. replaced by $d\xi_1, d\xi_2, \ldots d\xi_{\rho}$.

So we find,

$$W = \sqrt{\frac{E}{\pi^{\rho}}} \,.\, e^{-\left(\sum\limits_{1}^{\rho} b_{jj} \xi_j^2 + 2 \sum\limits_{1}^{\rho} b_{jk} \xi_j \xi_k\right)} \prod_{1}^{\rho} d\xi_j \times$$

$$\times \underset{x_{h(h=\rho+1,\ldots\sigma)}}{\int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty}} \sqrt{\frac{\prod\limits_{\rho+1}^{\sigma} b_{hh}}{\pi^{\sigma-\rho}}} \,.\, e^{-\sum\limits_{\rho+1}^{\sigma} b_{hh} x_h^2} \,.\, \prod_{\rho+1}^{\sigma} dx_h =$$

$$= \sqrt{\frac{E}{\pi^{\rho}}} \,.\, e^{-\left(\sum\limits_{1}^{\rho} b_{jj} \xi_j^2 + 2 \sum\limits_{1}^{\rho} b_{jk} \xi_j \xi_k\right)} \prod_{1}^{\rho} d\xi_j\,.$$

We have already calculated the coefficients b_{jk}, that is to say, expressed them in terms of the coefficients of the given equations of substitution. Their determinant E is consequently also known. For this latter, however, a simpler expression may be deduced. In order to find it we start from the relation

$$E = \frac{|b_{jk}|}{\prod\limits_{\rho+1}^{\sigma} b_{hh}} = \frac{1}{\Delta^2 \prod\limits_{\rho+1}^{\sigma} b_{hh}}\,.$$

Now $b_{hh} = \frac{1}{\Delta^2} \sum\limits_{i=1}^{\sigma} A_{hi}^2$ and $b_{hk} = \frac{1}{\Delta^2} \sum\limits_{i=1}^{\sigma} A_{hi} A_{ki} = 0$ (for $h = \varrho+1, \ldots \sigma$).

Consequently we have

$$\prod_{\rho+1}^{\sigma} b_{hh} = \begin{vmatrix} b_{\rho+1,\rho+1}, & 0 & , \ldots 0 \\ 0 & , b_{\rho+2,\rho+2}, & \ldots 0 \\ \vdots & \vdots & \\ 0 & , 0 & , \ldots b_{\sigma\sigma} \end{vmatrix} = \begin{vmatrix} b_{\rho+1,\rho+1}, & b_{\rho+1,\rho+2}, & \ldots b_{\rho+1,\sigma} \\ b_{\rho+2,\rho+1}, & b_{\rho+2,\rho+2}, & \ldots b_{\rho+2,\sigma} \\ \vdots & \vdots & \vdots \\ b_{\sigma,\rho+1} & , b_{\sigma,\rho+2} & , \ldots b_{\sigma\sigma} \end{vmatrix} =$$

$$= \frac{1}{\Delta^{2(\sigma-\rho)}} \begin{vmatrix} \Sigma A_{\rho+1,i}^2 & , \Sigma A_{\rho+1,i} \Sigma A_{\rho+2,i} & , \ldots \Sigma A_{\rho+1,i} A_{\sigma i} \\ \Sigma A_{\rho+2,i} A_{\rho+1,i} & , \Sigma A_{\rho+2,i}^2 & , \ldots \Sigma A_{\rho+2,i} A_{\sigma i} \\ \vdots & \vdots & \vdots \\ \Sigma A_{\sigma i} A_{\rho+1,i} & , \Sigma A_{\sigma i} A_{\rho+2,i} & , \ldots \Sigma A_{\sigma i}^2 \end{vmatrix} =$$

$$= \frac{(-1)^{\sigma\rho}}{\Delta^{2(\sigma-\rho)}} \begin{vmatrix} A_{\rho+1,1}, & A_{\rho+1,2}, & \ldots A_{\rho+1,\sigma}, & 0 & , 0 & , \ldots 0 \\ A_{\rho+2,1}, & A_{\rho+2,2}, & \ldots A_{\rho+2,\sigma}, & 0 & , 0 & , \ldots 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ A_{\sigma 1} & , A_{\sigma 2} & , \ldots A_{\sigma\sigma} & , 0 & , 0 & , \ldots 0 \\ -1 & , 0 & , \ldots 0 & , A_{\rho+1,1} & , A_{\rho+2,1} & , \ldots A_{\sigma 1} \\ 0 & , -1 & , \ldots 0 & , A_{\rho+1,2} & , A_{\rho+2,2} & , \ldots A_{\sigma 2} \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & , 0 & , \ldots -1 & , A_{\rho+1,\sigma} & , A_{\rho+2,\sigma} & , \ldots A_{\sigma\sigma} \end{vmatrix} \begin{array}{l} {}^{1)}\ R_1 \\ R_2 \\ \\ R_{\sigma-\rho} \\ R'_1 \\ R'_2 \\ \vdots \\ R'_\sigma \end{array}$$

or

$$\prod_{\rho+1}^{\sigma} b_{hh} = \frac{+1}{\Delta^{2(\sigma-\rho)}} \times \Sigma \begin{vmatrix} A_{\rho+1,r_{\rho+1}}, & A_{\rho+1,r_{\rho+2}}, & \ldots A_{\rho+1,r_\sigma} \\ A_{\rho+2,r_{\rho+1}}, & A_{\rho+2,r_{\rho+2}}, & \ldots A_{\rho+2,r_\sigma} \\ \vdots & \vdots & \\ A_{\sigma,r_{\rho+1}} & , A_{\sigma,r_{\rho+2}} & , \ldots A_{\sigma,r_\sigma} \end{vmatrix}^2$$

But

$$\begin{vmatrix} A_{\rho+1,r_{\rho+1}}, & \ldots A_{\rho+1,r_\sigma} \\ \vdots & \\ A_{\sigma,r_{\rho+1}} & , \ldots A_{\sigma,r_\sigma} \end{vmatrix}$$

is the minor of the reciprocal determinant $\overline{\Delta}$, which corresponds to the complementary minor of

$$D = \begin{vmatrix} a_{1r_1} & , a_{1r_2} & , \ldots a_{1r_\rho} \\ a_{2r_1} & , a_{2r_2} & , \ldots a_{2r_\rho} \\ \vdots & \vdots & \vdots \\ a_{\rho r_1} & , a_{\rho r_2} & , \ldots a_{\rho r_\rho} \end{vmatrix},$$

---

1) This reduction is easily controlled by first multiplying the rows $R'_1, R'_2, \ldots R'_\sigma$ resp. by $A_{\rho+1,1}, A_{\rho+1,2}, \ldots A_{\rho+1,\sigma}$ and adding all these products to R_1; then by multiplying the same rows resp. by $A_{\rho+2,1}, A_{\rho+2,2}, \ldots A_{\rho+2,\sigma}$ and adding these products to R_2, etc

if $r_1, r_2, \ldots r_\rho, r_{\rho+1}, \ldots r_\sigma$ represents a permutation of the numbers $1, 2, \ldots \sigma$. Apparently this last minor is again a determinant D of the ϱ^{th} order of the matrix M. Hence we have

$$\begin{vmatrix} A_{\rho+1,r_{\rho+1}}, & \ldots & A_{\rho+1,r_\sigma} \\ \vdots & & \vdots \\ A_{\sigma,r_{\rho+1}}, & \ldots & A_{\sigma,r_\sigma} \end{vmatrix} = \Delta^{\sigma-\rho-1} \times D$$

and

$$\prod_{\rho+1}^{\sigma} b_{hh} = \frac{1}{\Delta^{2(\sigma-\rho)}} \cdot \Sigma \left(\Delta^{\sigma-\rho-1} D\right)^2 = \frac{\Sigma D^2}{\Delta^2},$$

so that

$$E = \frac{1}{\Sigma D^2}.$$

So our result is:

$$W = \sqrt{\frac{E}{\pi^\rho}} \cdot e^{-\left(\sum_1^\rho b_{jj}\xi_j^2 + 2\sum_1^\rho b_{jk}\xi_j\xi_k\right)} \prod_1^\rho d\xi_j,$$

in which

$$b_{jk} = (-1)^{j+k} \frac{\Sigma D_j D_k}{\Sigma D^2} \qquad \left(\begin{matrix} j \\ k \end{matrix}\right\} = 1, 2, \ldots \varrho\Bigg)$$

and

$$E = \frac{1}{\Sigma D^2},$$

while D represents a determinant of the ϱ^{th} order of the matrix

$$M = \begin{vmatrix} a_{11}, & a_{12}, & \ldots & a_{1\sigma} \\ a_{21}, & a_{22}, & \ldots & a_{2\sigma} \\ \vdots & \vdots & & \vdots \\ a_{\rho 1}, & a_{\rho 2}, & \ldots & a_{\rho\sigma} \end{vmatrix}$$

and D_j a determinant of the $(\varrho-1)^{th}$ order of the matrix M_j, which is obtained by omitting the row $a_{j1}, a_{j2}, \ldots a_{j\sigma}$ in M.

Moreover the two determinants D_j and D_k, in the products are built up from the same columns of M.

Returning now to the coefficients α_{ji} we have only to write

$$a_{ji} = \frac{\alpha_{ji}}{h_i}.$$

Denoting by $\overline{D}, \overline{D}_j, \overline{D}_k$ the determinants in the coefficients α_{ji}, corresponding to D, D_j and D_k we have

$$D = \begin{vmatrix} a_{1r_1}, & a_{1r_2}, & \ldots a_{1r_\rho} \\ \vdots & & \\ a_{\rho r_1}, & a_{\rho r_2}, & \ldots a_{\rho r_\rho} \end{vmatrix} = \frac{\overline{D}}{h_{r_1} h_{r_2} \ldots h_{r_\rho}},$$

$$D_j = \begin{vmatrix} a_{1r_1}, & a_{1r_2}, & \ldots a_{1r_{\rho-1}} \\ \vdots & & \\ a_{j-1,r_1}, & a_{j-1,r_2}, & \ldots a_{j-1,r_{\rho-1}} \\ a_{j+1,r_1}, & a_{j+1,r_2}, & \ldots a_{j+1,r_{\rho-1}} \\ \vdots & \vdots & \vdots \\ a_{\rho r_1}, & a_{\rho r_2}, & \ldots a_{\rho r_{\rho-1}} \end{vmatrix} = \frac{\overline{D}_j}{h_{r_1} h_{r_2} \ldots h_{r_{\rho-1}}}$$

$$D_k = \frac{\overline{D}_k}{h_{r_1} h_{r_2} \ldots h_{r_{\rho-1}}},$$

or, if we introduce the mean errors ε_i by means of the formulae

$$h_i = \frac{1}{\varepsilon_i \sqrt{2}},$$

$$D = 2^{\frac{\rho}{2}} \varepsilon_{r_1} \varepsilon_{r_2} \ldots \varepsilon_{r_\rho} \overline{D}\,;\; D_j = 2^{\frac{\rho-1}{2}} \varepsilon_{r_1} \varepsilon_{r_2} \ldots \varepsilon_{r_{\rho-1}} \overline{D}_j\,;\; D_k = 2^{\frac{\rho-1}{2}} \varepsilon_{r_1} \varepsilon_{r_2} \ldots \varepsilon_{r_{\rho-1}} \overline{D}_k.$$

Before applying these results to questions concerning correlation we shall first deduce simple expressions for the minors B_{jk} of the coefficients b_{jk} in the determinant E.

If we represent the minor of b_{jk} in the determinant

$$|b_{jk}| = \begin{vmatrix} b_{11}, & b_{12}, & \ldots b_{1\sigma} \\ \vdots & \vdots & \vdots \\ b_{1\sigma}, & b_{2\sigma}, & \ldots b_{\sigma\sigma} \end{vmatrix} = \frac{1}{\Delta^2} = \prod_{\rho+1}^{\sigma} b_{hh} \times E = \frac{\prod_{\rho+1}^{\sigma} b_{hh}}{\Sigma D^2}$$

by β_{jk}, then for $j \leqq \varrho$, $k \leqq \varrho$:

$$B_{jk} = \frac{\beta_{jk}}{\prod_{\rho+1}^{\rho} b_{hh}} = \frac{\Delta^2}{\Sigma D^2} \cdot \beta_{jk}.$$

Now

$$\beta_{jk} = \frac{(-1)^{j+k}}{\Delta^{2(\sigma-1)}} \begin{vmatrix} \Sigma A_{1i}^2 & , \Sigma A_{1i} A_{2i} & ,\ldots \Sigma A_{1i} A_{j-1,i} & , \Sigma A_{1i} A_{j+1,i} & ,\ldots \Sigma A_{1i} A_{\sigma i} \\ \Sigma A_{2i} A_{1i} & , \Sigma A_{2i}^2 & ,\ldots \Sigma A_{2i} A_{j-1,i} & , \Sigma A_{2i} A_{j+1,i} & ,\ldots \Sigma A_{2i} A_{\sigma i} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \Sigma A_{k-1,i} A_{1i} & , \Sigma A_{k-1,i} A_{2i} & ,\ldots \Sigma A_{k-1,i} A_{j-1,i} & , \Sigma A_{k-1,i} A_{j+1,i} & ,\ldots \Sigma A_{k-1,i} A_{\sigma i} \\ \Sigma A_{k+1,i} A_{1i} & , \Sigma A_{k+1,i} A_{2i} & ,\ldots \Sigma A_{k+1,i} A_{j-1,i} & , \Sigma A_{k+1,i} A_{j+1,i} & ,\ldots \Sigma A_{k+1,i} A_{\sigma i} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \Sigma A_{\sigma i} A_{1i} & , \Sigma A_{\sigma i} A_{2i} & ,\ldots \Sigma A_{\sigma i} A_{j-1,i} & , \Sigma A_{\sigma i} A_{j+1,i} & ,\ldots \Sigma A_{\sigma i}^2 \end{vmatrix} =$$

$$
=\frac{+1}{\Delta^{2(\sigma-1)}}\begin{vmatrix}
A_{11} & A_{12} & \ldots A_{1\sigma} & 0 & 0 & \ldots 0 & 0 & \ldots 0 \\
A_{21} & A_{22} & \ldots A_{2\sigma} & 0 & 0 & \ldots 0 & 0 & \ldots 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
A_{k-1,1} & A_{k-1,2} & \ldots A_{k-1,\sigma} & 0 & 0 & \ldots 0 & 0 & \ldots 0 \\
A_{k+1,1} & A_{k+1,2} & \ldots A_{k+1,\sigma} & 0 & 0 & \ldots 0 & 0 & \ldots 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
A_{\sigma 1} & A_{\sigma 2} & \ldots A_{\sigma\sigma} & 0 & 0 & \ldots 0 & 0 & \ldots 0 \\
-1 & 0 & \ldots 0 & A_{11} & A_{21} & \ldots A_{j-1,1} & A_{j+1,1} & \ldots A_{\sigma 1} \\
0 & -1 & \ldots 0 & A_{12} & A_{22} & \ldots A_{j-1,2} & A_{j+1,2} & \ldots A_{\sigma 2} \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & \ldots -1 & A_{1\sigma} & A_{2\sigma} & \ldots A_{j-1,\sigma} & A_{j+1,\sigma} & \ldots A_{\sigma\sigma}
\end{vmatrix} =
$$

$$
=\frac{(-1)^{j+k}}{\Delta^{2(\sigma-1)}}\sum_{l=1}^{\sigma}\begin{vmatrix}
A_{11} & A_{12} & A_{1,l-1} & A_{1,l+1} & \ldots A_{1\sigma} \\
A_{21} & A_{22} & A_{2,l-1} & A_{2,l+1} & \ldots A_{2\sigma} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
A_{k-1,1} & A_{k-1,2} & A_{k-1,l-1} & A_{k-1,l+1} & \ldots A_{k-1,\sigma} \\
A_{k+1,1} & A_{k+1,2} & A_{k+1,l-1} & A_{k+1,l+1} & \ldots A_{k+1,\sigma} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
A_{\sigma 1} & A_{\sigma 2} & A_{\sigma,l-1} & A_{\sigma,l+1} & \ldots A_{\sigma\sigma}
\end{vmatrix} \times
$$

$$
\times\begin{vmatrix}
A_{11} & A_{21} & \ldots A_{j-1,1} & A_{j+1,1} & \ldots A_{\sigma 1} \\
A_{12} & A_{22} & \ldots A_{j-1,2} & A_{j+1,2} & \ldots A_{\sigma 2} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
A_{1,l-1} & A_{2,l-1} & \ldots A_{j-1,l-1} & A_{j+1,l-1} & \ldots A_{\sigma,l-1} \\
A_{1,l+1} & A_{2,l+1} & \ldots A_{j-1,l+1} & A_{j+1,l+1} & \ldots A_{\sigma,l+1} \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
A_{1\sigma} & A_{2\sigma} & \ldots A_{j-1,\sigma} & A_{j+1,\sigma} & \ldots A_{\sigma\sigma}
\end{vmatrix} =
$$

$$
=\frac{+1}{\Delta^{2(\sigma-1)}}\cdot\Delta^{2(\sigma-2)}\sum_{l=1}^{\sigma}a_{jl}a_{kl}=\frac{+\sum_{l=1}^{\sigma}a_{jl}a_{kl}}{\Delta^2}.
$$

Consequently we find

$$
B_{jk}=\frac{\Delta^2}{\Sigma D^2}\beta_{jk}=\frac{+\sum_{l=1}^{\sigma}a_{jl}a_{kl}}{\Sigma D^2},
$$

and in particular

$$
B_{jj}=\frac{\sum_{l=1}^{\sigma}a_{jl}^2}{\Sigma D^2}.
$$

(*To be continued*).

Chemistry. — "*Equilibria in ternary systems.* XIV. By Prof. SCHREINEMAKERS.

(Communicated in the meeting of March 28, 1914).

After the previous discussion of the saturationcurves under their own vapourpressure and of the boilingpointcurves of a component, we must yet deduce its solutionpaths under its own vapour-pressure. As, however, we discussed already formerly those of binary and ternary compounds the reader may easily deduce those of a component.

In the previous communications VII—X we have discussed the fourphase-equilibrium $F + F' + L + G$; for this we have assumed that F and F' are both ternary compounds. It is, however, easily seen that these considerations apply also to binary and unary substances, provided that F and F' contain together the three components; the line FF' is then situated, perhaps its extremities excepted, completely within the componentstriangle. Then the liquid contains also the three components, so that the quantity of none of them can approach to zero in it. When F and F' contain together only two components, the line FF' coincides with one of the sides of the componentstriangle. The quantity of one of the components may then approach to zero in the liquid and in the vapour, so that we must contemplate this case separately.

When we take e. g. the ternary equilibrium $B + C + L + G$, it is evident that the quantity of A can become equal to zero in the liquid and in the vapour. If the liquid and the vapour, in which the quantity of one of the components becomes equal to zero, is represented by L_0 and G_0, then the binary equilibrium $B + C + L_0 + G_0$ arises. Herein L_0 is the eutectical liquid under its own vapour-pressure of the binary system $B + C$; G_0 is the corresponding vapour; the corresponding temperature and pressure we call T_0 and P_0. The ternary equilibrium $B + C + L + G$ terminates, therefore, when the quantity of A becomes zero, at the temperature T_0 and under the pressure P_0 in the binary eutectical point with the phases $B + C + L_0 + G_0$.

Reversally we may also say that by addition of A the fourphase-equilibrium $B + C + L + G$ proceeds from the binary eutectical point with the phases $B + C + L_0 + G_0$.

When we take a eutectical point $B + C + L_0$ under a constant pressure, so that no vapour occurs, the threephaseequilibrium $B + C + L$ is formed on addition of A and the eutectical temperature is always lowered. From this naturally the question follows:

what influence has the addition of a new substance A on the temperature T_0 and the pressure P_0 of the eutectical point under its own vapourpressure with the phases $B+C+L_0+G_0$.

We may put this question also more generally; for this we replace the eutectical point with the phases $B+C+L_0+G_0$ by a quadruplepoint with the phases $F+F'+L_0+G_0$; F and F' are then either the components B and C or binary compounds of B and C.

When we take a constant pressure so high, that the vapour disappears, and when we add the substance A to the equilibrium $F+F'+L_0$ then the temperature is lowered. We may express this also in the following way: the common meltingpoint or point of inversion of two substances is lowered under a constant pressure by addition of a third substance [1]).

We now must put the question: what influence has the addition of a new substance A on the temperature T_0 and on the pressure P_0 of the quadruplepoint with the phases $F+F'+L_0+G_0$.

Firstly we shall consider the general case treated in communication VIII more in detail. Instead of the equations (2), (3), and (4) (VIII) we write:

$$[(x-\alpha)r+(y-\beta)s]\,dx+[(x-\alpha)s+(y-\beta)t]\,dy=AdP-BdT\ . \quad (1)$$

$$[(x_1-\alpha)r+(y_1-\beta)s]dx+[(x_1-\alpha)s+(y_1-\beta)t]dy=(A+C)\,dP-(B+D)dT \quad (2)$$

$$[(\alpha'-\alpha)r+(\beta'-\beta)s]dx+[(\alpha'-\alpha)s+(\beta'-\beta)t]dy=(A-A')\,dP-(B-B')dT\ . \quad (3)$$

We find from (1) and (3), eliminating dy:

$$\left.\begin{aligned} E(rt-s^2)dx = {} & [\{(\alpha'-x)A+(x-\alpha)A'\}\,s+\{(\beta'-y)A+(y-\beta)A'\}t]\,dP \\ & -[\{(\alpha'-x)B+(x-\alpha)B'\}\,s+\{(\beta'-y)B+(y-\beta)B'\}t]\,dT \end{aligned}\right\} \quad (4)$$

We find from (2) and (3):

$$\left.\begin{aligned} & E_1\,(rt-s^2)\,dx = \\ & [\{(\alpha'-x_1)A+(x_1-\alpha)A'+(\alpha'-\alpha)C\}s+\{(\beta'-y_1)A+(y-\beta)A'+(\beta'-\beta)C\}t]dP \\ & -[\{(\alpha'-x_1)B+(x_1-\alpha)B'+(\alpha'-\alpha)D\}s+\{(\beta'-y_1)B+(y-\beta)B'+(\beta'-\beta)D\}t]dT \end{aligned}\right\} \quad (5)$$

Herein E is equal to:

$$(\alpha'-x)(\beta-y)+(x-\alpha)(\beta'-y)=(\beta'-\beta)(x-\alpha)+(\alpha'-\alpha)(\beta-y)=$$
$$=(\beta'-\beta)(x-\alpha')+(\alpha'-\alpha)(\beta'-y).$$

We find E_1 by substituting in E x_1 and y_1 for x and y. For the sake of abbreviation we put the following:

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[1]) F. A. H. SCHREINEMAKERS. Heterog. Gleichgewichte III'.

$$\left.\begin{aligned}(\alpha'-\alpha)\,V+(x-\alpha')\,v+(\alpha-x)\,v'+E\frac{\partial V}{\partial y}&=(\alpha'-\alpha)\,V_y\\(\beta'-\beta)\,V+(y-\beta')\,v+(\beta-y)\,v'-E\frac{\partial V}{\partial x}&=(\beta'-\beta)\,V_x\\(\alpha'-\alpha)\,H+(x-\alpha')\,\eta+(\alpha-x)\,\eta'+E\frac{\partial H}{\partial y}&=(\alpha'-\alpha)\,H_y\\(\beta'-\beta)\,H+(y-\beta')\,\eta+(\beta-y)\,\eta'-E\frac{\partial H}{\partial x}&=(\beta'-\beta)\,H_x\end{aligned}\right\}\,.\quad(6)$$

When we replace E, V, H, x and y by E_1, V_1, H_1, x_1 and y_1 $\left(\frac{\partial V}{\partial y}, \frac{\partial V}{\partial x}\right.$ etc. rest unchanged$\Big)$ we obtain the corresponding quantities $V_{1.y}$, $V_{1.x}$, $H_{1,y}$ and $H_{1.x}$.

The following relations exist between these eight quantities, as we may easily deduce.

$$\left.\begin{aligned}E_1 V_y-EV_{1.y}&=E_1 V_x-EV_{1.x}\\E_1 \theta_y-EH_{1.y}&=E_1 H_x-EH_{1.x}\end{aligned}\right\}\,.\;.\;.\;.\;.\;.\quad(7)$$

We find another relation by eliminating E_1 and E from both these equations.

Substituting in (4) and (5) their values for A, B etc., we find with the aid of (6):

$$\left.\begin{aligned}E\,(rt-s^2)\,dx=&\,[(\alpha'-\alpha)\,V_y\,.\,s+(\beta'-\beta)\,V_x\,.\,t]\,dP\\&-[(\alpha'-\alpha)\,H_y\,.\,s+(\beta'-\beta)\,H_x\,.\,t]\,dT\end{aligned}\right\}\,.\quad(8)$$

$$\left.\begin{aligned}E_1\,(rt-s^2)\,dx=&\,[(\alpha'-\alpha)\,V_{1.y}\,.\,s+(\beta'-\beta)\,V_{1.x}\,.\,t]\,dP\\&-[(\alpha'-\alpha)\,H_{1.y}\,s+(\beta'-\beta)\,H_{1.x}\,.\,t]\,dT\end{aligned}\right\}\,.\quad(9)$$

Eliminating dx from (8) and (9) we find, when we make use of the relations (7):

$$\frac{dP}{dT}=\frac{H_{1.y}-\frac{E_1}{E}\,.\,H_y}{V_{1.y}-\frac{E_1}{E}\,.\,V_y}=\frac{H_{1.x}-\frac{E_1}{E}\,.\,H_x}{V_{1.x}-\frac{E_1}{E}\,.\,V_x}\;.\;.\;.\;.\;.\quad(10)$$

Herein H_y, H_x etc. have the meaning indicated in (6); from (10) it follows however, that this is also true when the term, in which E or E_1 occurs, is omitted in each of the eight relations (6).

Further we may deduce from (8) and (9):

$$\frac{dP}{dx}=\frac{(rt-s^2)E\left(H_{1.x}-\frac{E_1}{E}\,H_x\right)}{(\alpha'-\alpha)(V_yH_{1\,y}-V_{1.y}H_y)s+(\beta'-\beta)(V_xH_{1.x}-V_{1.x}H_x)t}\;.\quad(11)$$

$$\frac{dT}{dx}=\frac{(rt-s^2)E\left(V_{1.x}-\frac{E_1}{E}\,V_x\right)}{N}\;.\;.\;.\;.\;.\;.\quad(12)$$

In (12) N indicates the same denominator as in (11).

Let us now consider the case that both the solid substances of the equilibrium $F + F' + L + G$ are binary compounds of B and C. We must then put $\alpha = 0$ and $\alpha' = 0$. As E becomes $= (\beta' - \beta)\, x$ and $E_1 = (\beta' - \beta)\, x_1$, it follows from (10), (11) and (12):

$$\frac{dP}{dT} = \frac{H_{1.x} - \dfrac{x_1}{x} H_x}{V_{1.x} - \dfrac{x_1}{x} V_x} \quad \ldots\ldots\ldots\ldots \quad (13)$$

$$\frac{dP}{dx} = \frac{(rt - s^2)x\left(H_{1.x} - \dfrac{x_1}{x} H_x\right)}{(V_x H_{1.x} - V_{1.x} H_x)t} \quad \ldots\ldots\ldots \quad (14)$$

$$\frac{dT}{dx} = \frac{(rt - s^2)x\left(V_{1.x} - \dfrac{x_1}{x} V_x\right)}{(V_x H_{1.x} - V_{1.x} H_x)t} \quad \ldots\ldots\ldots \quad (15)$$

Let us now consider the terminating point of the ternary equilibrium $F + F' + L + G$ in the quadruplepoint $F + F' + L_0 + G_0$. For this we make in the previous equations x and x_1 approach to zero. As $Lim\; rx = RT$ it follows:

$$\frac{dP}{dT} = \frac{H_{1.x} - \left(\dfrac{x_1}{x}\right)_0 H_x}{V_{1.x} - \left(\dfrac{x_1}{x}\right)_0 V_x} \quad \ldots\ldots\ldots \quad (16)$$

$$\frac{dP}{dx} = \frac{RT\left[H_{1.x} - \left(\dfrac{x_1}{x}\right)_0 H_x\right]}{V_x H_{1.x} - V_{1.x} H_x} \qquad \frac{dT}{dx} = \frac{RT\left[V_{1.x} - \left(\dfrac{x_1}{x}\right)_0 V_x\right]}{V_x H_{1.x} - V_{1.x} H_x} \quad (17)$$

Herein $\left(\dfrac{x_1}{x}\right)_0$ is the value which $\dfrac{x_1}{x}$ assumes for $x = 0$ and $x_1 = 0$.

Further is:

$$(\beta' - \beta)\, V + (y - \beta')\, v + (\beta - y)\, v' = (\beta' - \beta)\, V_x \quad . \quad (18)$$

$$(\beta' - \beta)\, V_1 + (y_1 - \beta')\, v + (\beta - y_1)\, v' = (\beta' - \beta)\, V_{1.x} \quad . \quad (19)$$

$$(\beta' - \beta)\, H + (y - \beta')\, \eta + (\beta - y)\, \eta' = (\beta' - \beta)\, H_x \quad . \quad (20)$$

$$(\beta' - \beta)\, H_1 + (y_1 - \beta')\, \eta + (\beta - y_1)\, \eta' = (\beta' - \beta)\, H_{1.x} \quad . \quad (21)$$

wherein to all quantities (y, y_1, V, V_1, etc.) we must give the values, which they have in the quadruplepoint $F + F' + L_0 + G_0$. Herein L_0 has the composition: y quantities of $B + (1 - y)$ quant. of C; G_0 has the composition: y_1 quant. of $B + (1 - y_1)$ quant. of C.

Between the three phases F, F' and L_0 always may occur the reaction:

$(\beta'-\beta)$ quant. of $L_0+(\gamma-\beta')$ quant. of $F+(\beta-\gamma)$ quant. of $F'=0$ (22)
in which always one of the coefficients is negative. This reaction represents, according to the sign of the coefficients:

1. a congruent melting or solidification of $F+F'$ viz. the reaction $F+F' \rightleftarrows L_0$.

2. an incongruent melting or solidification of $F+F'$ viz. the reaction $F \rightleftarrows F'+L_0$ or $F' \rightleftarrows F+L_0$.

Consequently the incongruent melting or solidification of $F+F'$ means: the inversion of F in F' or reversally, by the side of liquid and vapour.

From (18) and (20) it follows that V_x represents the change of volume and H_x the change of entropy, when one quantity of vapour is formed at this reaction. Therefore, V_x is the increase of volume, H_x the increase of entropy at the congruent or incongruent melting of $F+F'$.

Between the three phases F, F' and G_0 the reaction:

$(\beta'-\beta)$ *quant. of* $G_0+(\gamma_1-\beta')$ *quant. of* $F+(\beta-\gamma)$ *quant. of* $F'=0$ (23)

may take place. From (19) and (21) it follows that $V_{1.x}$ represents the increase of volume, $H_{1.x}$ the increase of entropy when one quantity of vapour is formed at the reaction (23). $V_{1.x}$ is, therefore, the increase of volume, $H_{1.x}$ the increase of entropy at the congruent or incongruent sublimation of $F+F'$.

If we call W_x the (congruent or incongruent) heat of melting, and $W_{1.x}$ the (congruent or incongruent) heat of sublimation of $F+F'$, then $H_x=\frac{W_x}{T}$ and $H_{1.x}=\frac{W_{1.x}}{T}$. Further we put for the sake of abbreviation

$$V_{1.x}\,.\,W_x-V_x\,.\,W_{1.x}=K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (24)$$

When V_x, the change of volume on melting of $F+F'$ is positive, K is certainly positive; when, however V_x is negative, this form will nevertheless still be also positive, by reason of the great value of $V_{1.x}$ with respect to V_x. For this we shall assume K positive.

When we put further:

$$\Delta V=V_{1.x}-\left(\frac{x_1}{x}\right)_0 V_x \text{ and } \Delta W=W_{1.x}-\left(\frac{x_1}{x}\right)_0 W_x \quad . \quad . \qquad (25)$$

it follows:

$$T\frac{dP}{dT}=\frac{\Delta W}{\Delta V} \quad ; \quad \frac{dP}{dx}=-\frac{RT}{K}\,.\,\Delta W \quad ; \quad \frac{dT}{dx}=-\frac{RT^2}{K}\,\Delta V \,. \qquad (26)$$

$\left(\frac{x_1}{x}\right)_0$ is the ratio of the quantity of A in the vapour to that in the liquid when we add a little A to the binary equilibrium $F+F'+$

$+ L_0 + G_0$; we may call this ratio the limitratio of A in $F + F' + L_0 + G_0$.

Considering the cases $\left(\frac{x_1}{x}\right) < 1$ and $\left(\frac{x_1}{x}\right) > 1$ in connection with the values of $V_{1.x}$, V_x, $W_{1.x}$ and W_x (V_x can also be negative) it follows:

The P,T curve of the ternary equilibrium $F + F' + L + G$ ends in the quadruplepoint $F + F' + L_0 + G_0$; it is a curve ascendant with the temperature, when the limitratio of A is smaller or only a little larger than 1; it may have a point of maximumpressure when the limitratio of A is much greater than 1; it may have, besides the point of maximumpressure, also a point of maximumtemperature, when the limitratio of A is very large (e. g. larger than 10000) and when the volume increases at the congruent or incongruent melting of $F + F'$.

We may express the previous also in the following way:

The congruent or incongruent meltingpoint of two substances $(F + F')$ is always lowered by addition of a new substance, when we take the pressure constant; generally this is also the case when this addition takes place under its own vapourpressure. In the latter case the temperature may however, before it decreases, yet first rise a little. This can take place however only in the case that the limitratio $\left(\frac{x_1}{x}\right)_0$ of the new substance in $F + F' + L_0 + G_0$ is very large and when the volume increases at the formation of liquid from $F + F'$.

The vapourpressure of the congruent or incongruent meltingpoint, can by addition of the new substance according to the value of $\left(\frac{x_1}{x}\right)_0$, either decrease immediately or, before it decreases, firstly increase. This latter is certainly the case when the temperature increases also firstly, but it may also take place then, when the temperature decreases immediately.

Let us now consider the case that $\left(\frac{x_1}{x}\right)_0$ is exceedingly small or approaches to zero. This will be the case when the quantity of A is exceedingly small in the vapour, therefore, e. g. when A is a salt, very little or not volatile. From (25) and (26) then follows:

$$T\frac{dP}{dT} = \frac{W_{1.x}}{V_{1.x}} \quad ; \quad \frac{dP}{dx} = -\frac{RT}{K} W_{1.x} \quad ; \quad \frac{dT}{dx} = -\frac{RT^2}{K} V_{1.x} \quad . \quad (27)$$

As $W_{1.x}$ represents the (congruent or incongruent) heat of sublimation and $V_{1.x}$ the increase of volume at the (congruent or incongruent) sublimation of $F+F'$, $W_{1.x}$ and $V_{1.x}$ are both positive. Therefore, the equilibrium $F+F'+L+G$ proceeds from the quadruplepoint immediately towards lower temperatures and pressures. Let us imagine a P,T-diagram with the quadruplepoint $F+F'+$ $+L_0+G_0$. Four triplecurves proceed from this point viz. the (congruent or incongruent) binary meltingcurve $F+F'+L_0$, the (congruent or incongruent) binary sublimationcurve $F+F'+G_0$ and further the two binary solutioncurves under their own vapourpressure, viz. the curves $F+L_0+G_0$ and $F'+L_0+G_0$. When we draw in this P,T-diagram also the curve for the ternary equilibrium $F+F'+L+G$, this touches, according to (27) the binary sublimationcurve $F+F'+G_0$ in the quadruplepoint.

An example of this case will be found when we add a third substance, which is not volatile, to the equilibrium: $ICl+ICl_3+$ $+L_0+G_0$ occurring at $T_0=22{,}7°$ and under $P_0=42$ m.m., in which G_0 contains the two components I_2 and Cl_2. The same shall also be the case when we add a substance, which is not volatile, e.g. $NaCl$ or $NaNO_3$ to the equilibrium $Na_2SO_4.10H_2O+Na_2SO_4+$ $+L_0+G_0$ wherein G_0 consists only of water-vapour.

Let us now consider the case that $\left(\frac{x_1}{x}\right)_0$ is very large; as limitcase we shall assume $\left(\frac{x_1}{x}\right)_0$ infinitely large. From (25) and (26) then follows:

$$T\frac{dP}{dT}=\frac{W_x}{V_x} \quad \text{. . . . .} \quad (28)$$

As W_x represents the heat, required for the congruent or incongruent melting of $F+F'$, and V_x the increase of volume at this reaction, W_x is positive, while V_x may be as well positive as negative. Imagining in a P,T-diagram the quadruplepoint $F+F'+$ $+L_0+G_0$ and the binary (congruent or incongruent) meltingcurve $F+F'+L_0$, proceeding from this point the curve of the ternary equilibrium $F+F'+L+G$ will touch this binary meltingcurve in the quadruplepoint.

In the quadruplepoint $F+F'+L_0+G_0$ always between the phases L_0, G_0 and F the reaction:

$(y_1-\beta)$ quant. of L_0 + $(\beta-y)$ quant. of G_0 + $(y-y_1)$ quant. of $F=0$ (29)

may occur. The changes of entropy and of volume at this reaction are:

$$(y_1-\beta)\,H+(\beta-y)\,H_1+(y-y_1)\,\eta \quad \text{. . . . .} \quad (30)$$

$$(y_1-\beta)\,V+(\beta-y)\,V_1+(y-y_1)\,v \quad \text{. . . . . .} \quad (31)$$

It follows from the values of V_x, $V_{1.x}$, H_x, and $H_{1.x}$ [(18)—(21)] that we may also write for (30) and (31):

$$(\beta - y)\, H_{1.x} - (\beta - y_1)\, H_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (32)$$

and

$$(\beta - y)\, V_{1.x} - (\beta - y_1)\, V_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (33)$$

(30) and therefore also (32) represent the increase of entropy, when at the reaction between L_0, G_0, and F in all $\beta - y$ quantities of vapour are formed; (31) and (33) represent the change of volume at this reaction. From this it follows: when between the phases L_0, G_0, and F a reaction takes place, so that one quantity of vapour is formed, the increase of entropy is:

$$H_{1.x} - \frac{\beta - y_1}{\beta - y} H_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (34)$$

consequently the heat which is to be added:

$$W_{1.x} - \frac{\beta - y_1}{\beta - y} W_x . \quad . \quad . \quad . \quad . \quad , \quad . \quad . \quad . \qquad (35)$$

and the increase of volume:

$$V_{1x} - \frac{\beta - y_1}{\beta - y} V_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (36)$$

Let us now imagine in a P, T-diagram the quadruplepoint $F + F' + L_0 + G_0$ and the binary solutioncurve of F under its own vapourpressure, proceeding from this point, therefore, the curve $F + L_0 + G_0$, its direction in the quadruplepoint is fixed by

$$T \frac{dP}{dT} = \frac{W_{1.x} - \dfrac{\beta - y_1}{\beta - y} W_x}{V_{1.x} - \dfrac{\beta - y_1}{\beta - y} V_x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (37)$$

We imagine also in this P, T-diagram to be drawn the curve of the ternary equilibrium $F + F' + L + G$ proceeding from this quadruplepoint $F + F' + L_0 + G_0$. Its direction is fixed in this point by (25) and (26). When accidentally:

$$\left(\frac{x_1}{x}\right)_0 = \frac{\beta - y_1}{\beta - y} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (38)$$

both the curves will touch one another in the quadruplepoint.

The meaning of (38) is the following. We imagine in the concentration-diagram on the side BC the liquid of the quadruplepoint q. Through this point q runs a saturationcurve under its own vapourpressure and a boilingpointcurve of F. The meaning of (38) is that the point of maximum or minimum pressure or temperature falls exactly in q.

In the same way we find that in a P, T-diagram the binary solutioncurve under its own vapourpressure of F' proceeding from the quadruplepoint, therefore, curve $F' + L_0 + G_0$, and the curve of the ternary equilibrium $F + F' + L + G$ proceeding from this point touch one another when

$$\left(\frac{x_1}{x}\right)_0 = \frac{\beta' - y_1}{\beta' - y} \quad \ldots \ldots \ldots \ldots (39)$$

We can summarise the previous results in the following way. We imagine a P, T-diagram with the quadruplepoint $F + F' + L_0 + G_0$, the four triplecurves proceeding from this point and the curve of the ternary equilibrium $F + F' + L + G$ proceeding from this point. This last curve touches in the quadruplepoint:

the binary (congruent or incongruent) meltingcurve of $F + F'$ (curve $F + F' + L_0$) when $\left(\frac{x_1}{x}\right)_0 = \infty$

the binary (congruent or incongruent) sublimationcurve of $F + F'$ (curve $F + F' + G_0$) when $\left(\frac{x_1}{x}\right)_0 = 0$

the binary solutioncurve under its own vapourpressure of F (curve $F + L_0 + G_0$) when (38) is satisfied

the binary solutioncurve under its own vapourpressure of F' (curve $F' + L_0 + G_0$) when (39) is satisfied.

The above considerations apply of course also to the ternary cryohydric curves under their own vapourpressure. As in a binary cryohydric point under its own vapourpressure the equilibrium $F + Ice + L_0 + G_0$ occurs and as from this point the ternary cryohydric curve $F + Ice + L + G$ proceeds, we have to replace only F' by *Ice* in our previous considerations. Then we must equate β' to 0 in (18)—(21), (25) and (26); we then may summarise our previous results in the following way:

The cryohydric point of a substance is always lowered by addition of a new substance when we keep the pressure constant; generally this is also the case when this addition takes place under its own vapourpressure. In the latter case the temperature, however, may also firstly increase a little, before it decreases; this may take place however only then, when the limitratio $\left(\frac{x_1}{x}\right)_0$ of the new substance in $F + Ice + L_0 + G_0$ is very large and when the volume increases at the formation of liquid from $F + Ice$.

The vapourpressure of the cryohydric point, may, according to the value of $\left(\frac{x_1}{x}\right)_0$ by addition of a new substance either decrease immediately or, before it decreases, first increase. This latter is certainly the case when the temperature also increases a little at first, but it may also take place then when the temperature decreases immediately.

We have assumed in all our previous considerations of the equilibrium $F + F' + L + G$ that the four phases have a different composition; now we shall consider the case that two of these phases have the same composition. This will amongst others be the case when F and F' are modifications of the same solid substance or also when F or F' is one of the components and when the vapour consists only of this component. This latter is e. g. the case for the cryohydric curve under its own vapourpressure $F + Ice + L + G$ when of the three components only the water is volatile and the gasphase contains consequently only watervapour.

Let us first consider the latter case; we take, therefore, the cryohydric curve under its own vapourpressure $F + Ice + L + G$ and we preassume that the gas contains only watervapour. The results, therefore, of course remain also valid, when we replace the ice by another component. Now we must equate in our previous considerations $\alpha' = 0$, $\beta' = 0$, $x_1 = 0$ and $y_1 = 0$; from this follows: $E = \alpha y - \beta x$ and $E_1 = 0$, from (6) follows $V_{1x} = V_1 - v'$ and $H_{1x} = H_1 - \eta'$. Now it follows from (10):

$$\frac{dP}{dT} = \frac{H_{1x}}{V_{1x}} = \frac{H_1 - \eta'}{V_1 - v'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Herein H_1 and V_1 represent the entropy and the volume of the gas, therefore of the watervapour; η' and v' are the entropy and the volume of the *ice*. From this follows, therefore, that $\frac{dP}{dT}$ is the same for the ternary equilibrium $F + Ice + L + G$ and for the unary equilibrium $Ice +$ watervapour. This is evident, also without calculation; removing viz. from the ternary equilibrium $F + Ice + L + G$ the solid substance F and the liquid L, we retain, as G consists only of watervapour, the unary equilibrium *ice* + watervapour.

If we imagine the sublimationcurve of the *ice* and the cryohydric curve $F + ice + L + G$ to be drawn in a P,T-diagram the two curves must, therefore, coïncide. As the first curve is experimentally known, we know, therefore, also the curve $F + ice + L + G$.

A cryohydric curve under constant pressure (consequently the equilibrium $F + ice + L$) has in the concentrationdiagram the point of maximumtemperature in its point of intersection with the line, which joins the two solid phases F and *ice*. This is also the case with the cryohydric curve under its own vapourpressure. In the point of intersection of this curve with the line *F— ice* is viz. $\alpha y = \beta x$, therefore $E = 0$. From (11) and (12) it follows therefore, that $dP = 0$ and $dT = 0$. In this point of intersection pressure and temperature are, therefore, either maximum or minimum. In order to examine more in detail whether a maximum or a minimum occurs, we assume the conditions of equilibrium for the system $F + ice + L + G$.

These are:

$$\left.\begin{aligned} & x\frac{\partial Z}{\partial x} + y\frac{\partial Z}{\partial y} - Z + \zeta' = 0 \\ & \alpha\frac{\partial Z}{\partial x} + \beta\frac{\partial Z}{\partial y} + \zeta' - \zeta = 0 \text{ and } Z_1 - \zeta' = 0 \end{aligned}\right\} \quad . \quad . \quad . \quad (41)$$

Now it follows from the first of these conditions:

$$\left.\begin{aligned} & xr + ys)\, dx + (xs + yt)\, dy + \left(x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} - V + v'\right) dP \\ & -\left(x\frac{\partial H}{\partial x} + y\frac{\partial H}{\partial y} - H + \eta'\right) dT + \tfrac{1}{2}\left(r + x\frac{\partial r}{\partial x} + y\frac{\partial s}{\partial y}\right) dx^2 + \\ & +\left(s + x\frac{\partial r}{\partial y} + y\frac{\partial s}{\partial y}\right) dxdy + \tfrac{1}{2}\left(t + x\frac{\partial s}{\partial y} + y\frac{\partial t}{\partial y}\right) dy^2 + R = 0 \end{aligned}\right\} \quad (42)$$

From the second it follows:

$$\left.\begin{aligned} & (\alpha r + \beta s)\, dx + (\alpha s + \beta t)\, dy + \left(\alpha\frac{\partial V}{\partial x} + \beta\frac{\partial V}{\partial y} + v' - v\right) dP \\ & -\left(\alpha\frac{\partial H}{\partial x} + \beta\frac{\partial H}{\partial y} + \eta' - \eta\right) dT + \tfrac{1}{2}\left(\alpha\frac{\partial r}{\partial x} + \beta\frac{\partial s}{\partial y}\right) dx^2 \\ & + \left(\alpha\frac{\partial r}{\partial y} + \beta\frac{\partial s}{\partial y}\right) dxdy + \tfrac{1}{2}\left(\alpha\frac{\partial s}{\partial y} + \beta\frac{\partial t}{\partial y}\right) dy^2 + R' = 0 \end{aligned}\right\} \quad (43)$$

Herein R and R' contain terms with $dPdx$, $dTdx$ etc., which we may neglect as will appear later. From the third condition follows:

$$(V_1 - v')\, dP - (H_1 - \eta')\, dT = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

wherein the terms of higher order can also be neglected. As in the point of intersection of the curve with the line *F—Ice* $\alpha y = \beta x$, so we may substitute in (43) $\alpha = \lambda x$ and $\beta = \lambda y$.

When we subtract (42) from (43) after having multiplied (42) by λ, we find:

$$\left.\begin{aligned} & \{\lambda(V - v') + v' - v\}\, dP - \{\lambda(H - \eta') + \eta' - \eta\} dT \\ & = \tfrac{1}{2}\lambda(rdx^2 + 2sdxdy + tdy^2) + R'' \end{aligned}\right\} \quad . \quad . \quad . \quad (45)$$

Let us substitute the value of dy from (43) into (45); it is apparent from (45) that it is sufficient that:

$$(\alpha s + \beta t)dy = -(\alpha r + \beta s)dx$$

and that we may neglect the terms with dP, dT etc. We may write then for the second term of (45): $\frac{1}{2}\lambda Q \,.\, dx^2$, wherein Q is positive. From (6) it follows that we may write V_x and H_x for the coefficient of dP and dT; (45) passes into:

$$V_x \,.\, dP—H_x \,.\, dT = \tfrac{1}{2} \,.\, \frac{\alpha}{x} \,.\, Q \,.\, dx^2 . \quad \ldots \ldots \quad (46)$$

From (44) and (46) follows:

$$2x\,[H_x(V_1{}'-v')-V_x\,(H_1-\eta')]\,dP = -\,\alpha(H_1-\eta')\,Qdx^2 \quad . \quad (47)$$

$$2x\,[H_x(V_1-v')-\,V_x\,(H_1—\eta')]\,dT = -\,\alpha(V_1-v')\,Qdx^2 \quad . \quad (48)$$

As $V_1—v' = V_{1.x}$ and $H_1—\eta' = H_{1.x}$, we see from (24) that the coefficients of dP and dT in (47) and (48) are positive. Therefore, dP and dT are zero at first approximation, at second approximation negative so that pressure and temperature are maximum.

We may summarise the previous results in the following way: in a P,T-diagram the sublimationcurve of the *ice* and the cryohydric curve under its own vapourpressure ($F + ice + L + G$) coincide. The cryohydric curve under a constant pressure has its maximumtemperature in the pure solutionpoint of F; the cryohydric curve under its own vapourpressure has in this point its maximumtemperature and -pressure.

When F is a binary compound, we must in the previous considerations not only put $\alpha' = 0$, $\beta' = 0$, $x_1 = 0$ and $y_1 = 0$, but also $\alpha' = 0$. From this follows: $E = -\beta x$, $E_1 = 0$, $V_{1\,x} = V_1—v'$ and $H_{1.x} = H_1—\eta'$. From (10) again it follows that:

$$\frac{dP}{dT} = \frac{H_1—\eta'}{V_1-v'} \quad \ldots \ldots \ldots \quad (49)$$

so that in a P,T-diagram again the sublimationcurve of the ice and the cryohydric curve $F + Ice + L + G$ coincide.

Considering the cryohydric curve in the vicinity of the binary cryohydric point $F + ice + L_0 + G_0$, it follows from (25) and (26):

$$\frac{dP}{dx} = -\frac{RT}{K}\,W_{1.x} = -\frac{RT^2}{K}\,H_{1\,x} = -\frac{RT^2}{K}\,(H_1—\eta') \quad . \quad . \quad (50)$$

$$\frac{dT}{dx} = -\frac{RT^2}{K}\,V_{1\,x} = -\frac{RT^2}{K}\,(V_1-v') \quad \ldots \ldots \ldots \quad (51)$$

From the binary cryohydric point, therefore, pressure and temperature decrease along the cryohydric curve.

We can also obtain these results by substituting $Z = U + RTx \log x$ in the three equations (41).

Now we shall suppose that F and F' are modifications of a same substance, so that $F + F' + L + G$ represents the modificationcurve under its own vapourpressure and its corresponding vapourcurve. We put in the formulae (2)—(4) (VIII) $\alpha' = \alpha$ and $\beta' = \beta$. We then may write these:

$$(x-\alpha)r + (y-\beta)s]\, dx + [(x-\alpha)s + (y-\beta)t]\, dy = AdP - BdT. \quad (52)$$

$$\left.\begin{array}{c}[(x_1-\alpha)r + (y_1-\beta)s]\, dx + [(x_1-\alpha)s + (y_1-\beta)t]\, dy \\ = (A+C)\, dP - (B+D)dT\end{array}\right\} \quad . \quad . \quad (53)$$

$$(v'-v)\, dP - (\eta'-\eta)\, dT = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

Let us first take the substance F. The P,T-diagram of this substance was already discussed formerly and is drawn in fig. 3 (III) and 4 (IV). In fig. 1 arK represents the sublimationcurve, Fd the meltingcurve and KF a part of the limitcurve $mKFM$ of the substance F. We find also in fig. 1 the P,T-diagram of the substance F'; herein $a'rK'$ is the sublimationcurve, $F'd'$ the melting curve and $K'F'$ a part of the limitcurve $m'K'F'M'$ of the substance F'.

The two sublimationcurves touch one another in r; consequently in r the equilibrium $F+F'+G$ occurs, wherein G has the composition $F=F'$. Therefore from r also a curve rh proceeds, which represents the equilibrium $F+F'$. This curve may proceed from r as well towards higher as towards lower temperatures; in fig. 1 the first case has been assumed. It is apparent from the position of the different curves that we have assumed $v' > v$, $\eta' > \eta$, $V > v$ and $V > v'$.

From (54) it follows that $\frac{dP}{dT}$ for the equilibrium $F+F'+L+G$ and $F+F'$ is the same. This is also apparent without more explanation; when we remove viz. the liquid and the gas from

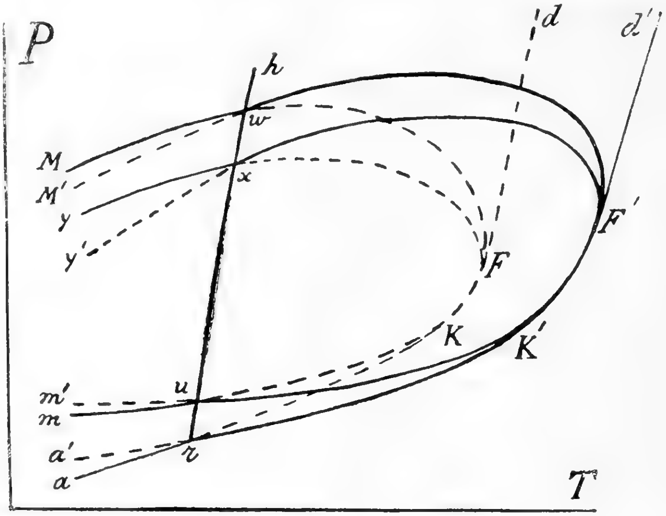

Fig. 1.

$F+F'+L+G$, then $F+F'$ remains. Therefore, in fig. 1 curve $F+F'+L+G$ must coincide with rh; it will, however, only partly cover this curve. It is represented in fig. 1 by uw, wherein u and w are the points of intersection of $mKFM$ and $m'K'F'M'$.

In order to see this we take any point x of the curve $F+F'+L+G$. When we remove F' and when we keep further the quantity of vapour always exceedingly small, the liquid L of the remaining equilibrium $F+L+G$ traces at change of temperature a solutionpath of F under its own vapourpressure. The P,T-curve of this path is represented in fig. 1 by $y\,x\,F$. When we remove F and when we keep again the quantity of vapour exceedingly small, the liquid L traces a solutionpath of F' on change of temperature; this is indicated in fig. 1 by $y'\,x\,F'$.

Only the part yx of the first solutionpath, only the part $x\,F'$ of the second represent stable conditions. Restricting ourselves to stable conditions, we may say therefore: from each point of the modificationcurve $F+F'+L+G$ one solutionpath of F proceeds towards lower temperatures, and one of F' towards higher temperatures. From this it follows that the one extremity of the modificationcurve must be situated in u, and the other in w.

In order to deduce the modificationcurve and its corresponding vapourcurve in the concentrationdiagram, we may act in a similar way as e.g. at the deduction of the saturationcurves under their own vapourpressure. When we take a definite T and P and when at this T and under this P a saturationcurve of F exists, this is circumphased; the same applies to that of F'. When at the assumed T and P the modification F is the stable one, its saturationcurve surrounds that of F'; when F' is the stable form, the saturationcurve of F' surrounds that of F.

The two saturationcurves can never intersect each other, they can completely coincide. This is the case when we choose P and T in such a way that they are in accordance with a point of curve $r\,h$ in fig. 1, so that the two modifications F and F' may exist by the side of one another. Then these two coinciding curves form the modificationcurve under a constant P and at a constant T; it represents the liquid L of the equilibrium $F+F'+L$.

Now we change not only the T or the P, but both together and in such a way that they are always in accordance with a point of the curve $r\,h$ in fig. 1; also we consider the vapourregion and the heterogeneous region $L—G$. Then we find easily that the modificationcurve under its own vapourpressure and its corresponding vapourcurve are circumphased.

It follows amongst others from the formulas (52)—(54) that this modificationcurve cannot go through the point $F=F'$; when we put herein $x=\alpha$ and $y=\beta$, it follows that

$$\frac{H-\eta}{V-v}=\frac{H-\eta'}{V-v'}=\frac{\eta'-\eta}{v'-v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

must be satisfied.

This means that the curves $Fd, F'd'$ and rh of fig. 1 touch one another in one point. Now it is apparent that these curves may intersect one another in one point. When viz. two of these curves intersect one another, necessarily the third goes also through this point of intersection; only very accidentally they can, however, touch one another. In the same way we find that also the corresponding vapourcurve cannot go through the point $F=F'$. From (52)—(54) it follows that dP and dT become zero at the same time and that this is the case when

$$\frac{y-\beta}{x-\alpha}=\frac{y_1-\beta}{x_1-\alpha} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

This means that the solid substance $(F=F')$, the liquid and the vapour are situated on a straight line. It is evident that on each closed modificationcurve two such points u and w occur and on the corresponding vapourcurve two corresponding points u_1 and w_1. Pressure and temperature of the equilibrium $F+F'+L_u+G_{u_1}$ are in accordance with point u of fig. 1, pressure and temperature of the equilibrium $F+F'+L_w+G_{w_1}$, with the point w of fig. 1.

From (54) it follows that the pressure can as well increase as decrease at increase of temperature; therefore we may distinguish two cases.

1) P- and T-maximum coincide and also P- and T-minimum.

2) P-maximum and T-minimum coincide and also P-minimum and T-maximum.

The case sub 1 occurs when the pressure increases at increase of temperature; curve rh is then situated as in fig. 1. The case sub 2 occurs when the pressure decreases at increase of temperature, curve rh proceeds then in fig. 1 from r towards lower temperatures.

Now we shall assume that F and consequently also F' is a binary compound of B and C; to the P, T diagram again then fig. 1 applies, in which now however the solutionpaths no longer touch the meltingcurve in F or F'.

In the concentrationdiagram the modificationcurve $F+F'+L+G$ ends in two points on the side BC, the same applies to its corresponding vapourcurve.

Let us assume that point F in fig. 3 (XI) represents the two modifications F and F' and that $h\,a\,b\,n$ is the modificationcurve and $h_1a_1b_1n_1$ the vapourcurve.

Therefore, in the binary system two temperatures and pressures of inversion occur, viz. in the points h and n. Considering the equilibria under a constant pressure, $T_h = T_n$; under their own vapour pressure, however T_h and T_n as well as P_h and P_n are different. The points h and n of fig. 3 (XI) resemble viz. u and w of fig. 1. Although solid substance, liquid and gas of the equilibrium $F+F'+L_h+G_{h_1}$ and $F+F'+L_n+G_{n_1}$ are represented by points of a straight line, yet in h and n $dP=0$ and $dT=0$ is not the case. In order to see this, we substitute in (52)—(54) $\alpha=0$; from this we find:

$$\frac{1}{RT}\cdot\left(\frac{dP}{dx}\right)_{x=0}=\frac{x_1}{x}\cdot\left(1-\frac{s}{s_1}\right)\frac{\eta'-\eta}{(\eta'-\eta)\Delta V-(v'-v)\Delta H} \quad . \quad . \quad (57)$$

$$\frac{1}{RT}\cdot\left(\frac{dT}{dx}\right)_{x=0}=\frac{x_1}{x}\left(1-\frac{s}{s_1}\right)\frac{v'-v}{(\eta'-\eta)\Delta V-(v'-v)\Delta H} \quad . \quad . \quad (58)$$

so that dP and dT in h and n are not zero. ΔV is the increase of volume and ΔH is the increase of entropy when between F, L, and G of the equilibrium $F+F'+L_n+G_{n_1}$ or $F+F'+L_h+G_{h_1}$ a reaction takes place, at which one volume of vapour is formed. [We may also replace in (57) and (58) ΔV and ΔH by $\Delta V'$ and $\Delta H'$, which indicate then the same increases when the phases F', L, and G react]. When in fig. 3 (XI) h and n are situated not too close to F, or in other words, when the temperatures of inversion T_h and T_n are situated not too close to the meltingpoint T_F, ΔV is >0 and large with respect to $v'-v$; the denominator of (57) and (58) is then generally positive.

That there may be accordance with fig. 1, we take first $v'>v$. In fig. 3 in the vicinity of h and h_1 (see $\Delta\, Faa_1$) $s>s_1$; in the vicinity of n and n_1 (see $\Delta\, Fbb_1$) $s<s_1$. From (57) and (58) now follows: P and T increase along the modificationcurve from n towards h. When we take $v'<v$ then it follows: T increases from h towards n, P from n towards h.

At last we may still consider the case, that F and consequently also F' is one of the components, e.g. B. The reader can easily draw himself the P,T-diagram, which is now simpler than in fig. 1. In the concentrationdiagram the modificationcurve ends then in two points, the one on BC and the other on BA. If we determine the modificationcurve under a constant pressure, T is the same in each point of this curve; in this case T and P will change however again

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along the curve from point to point and either in the same or in opposite direction.

When we determine, therefore, e.g. the temperature of inversion and pressure of inversion of rhombic in monoclinic sulfur, or of two modifications of KNO_3 etc. in a mixture of two solvents and under its own vapourpressure, this T and P of inversion change with the composition of the solvent. These changes are, however, very small, as it follows from the previous considerations.

(To be continued.)

Mathematics. — *"On the singular solutions of ordinary and partial differential equations of the first order"*. By Prof. Hk. de Vries and G. Schaake.

(Communicated in the meeting of March 28, 1914).

Introduction. If the complete integral of a partial differential equation of the first order with two independent variables, $F(x,y,z,p,q) = 0$ is represented by $f(x,y,z,c_1,c_2) = 0$, and if the result of the elimination of c_1 and c_2 from the three equations

$$f = 0 \quad , \quad \frac{\partial f}{\partial c_1} = 0 \quad , \quad \frac{\partial f}{\partial c_2} = 0$$

is called for the sake of brevity $E = 0$, the following peculiar phenomena may arise. If the general solution $f(x,y,c) = 0$, of an *ordinary* differential equation of the first order $F(x,y,p) = 0$, possesses a nodal locus, it belongs generally speaking to the result of elimination of c from the two equations

$$f = 0 \quad , \quad \frac{\partial f}{\partial c} = 0 \; ;$$

and only in *one* particular case it does not belong to it; with the partial equations it is just the reverse, at least if in this case the locus of the nodes consists of one or more *curves*; if there is a nodal *surface*, it does belong in general to $E = 0$, though there is a possibility that it does not.

It is a matter of course that all possible cases may be arrived at by a purely analytical method; but it appears that considerations derived from polydimensional geometry throw a vivid light on those various analytical possibilities and so to say increase the differences and render them more essential; to prove this is the aim of the following paragraphs.

§ 1. Let in the first place be given an ordinary differential equation of the 1st order

$$F(x, y, p) = 0,$$

with the general solution $f(x,y,u)=0$ (we represent, with a view to the geometrical interpretation that is to follow, the arbitrary constant by u), then the result of elimination $E=0$ of

$$f=0 \quad , \quad \frac{\partial f}{\partial u}=0$$

represents the locus of *those* points in the xy-plane, for which the equation $f(x,y,u)=0$, considered as an equation in u, possesses a double or multiple root, hence the locus of those points, through which *one* particular integral less passes than through an arbitrary point (if we restrict ourselves to a *double* root); it is obvious now to surmise that a point which is node of a definite particular integral, will belong to this locus, because the curve with the node passes twice through that point, but in general this is incorrect, as may appear from very simple instances. The equation

$$x^2-y^2-2x(x-yp)=R^2-2(x-yp)^2$$

has as general solution

$$x^2-y^2-2ax=R^2-2a^2,$$

in which a represents the arbitrary constant, consequently a system of equilateral hyperbolae. The result of elimination E of a from this last equation and its partial derivative with regard to a: gives,

$$E=x^2-2y^2-2R^2=0,$$

and this is really the envelope of the equilateral hyperbolae.

Let now $\frac{\partial f}{\partial x}=2x-2a=0$, and $\frac{\partial f}{\partial y}=-2y=0$, then we find that the point $x=a$, $y=0$ is a node for the particular integral which is determined by giving to a e.g. the value R, thus for the pair of straight lines

$$(x-R)^2-y^2=0;$$

but the node $x=R$, $y=0$ does apparently not lie on E. And in fact through the point $x=R$, $y=0$ passes not only the particular integral $a=R$, but also $a=0$ $(x^2-y^2=R^2)$, viz. two, just as through an arbitrary point.

What consequences has this for the differential equation?

By solving it with regard to p we find for each point the tangents of the integral curves passing through that point, so in our case 2; but in the point $x=R$, $y=0$ we must find 3 now, viz. the two 45°-lines, and the line parallel to the y-axis; hence the differential equation must disappear identically in this case, which occurs at once through substitution.

§ 2. A point satisfying the three equations

$$f(x,y,u)=0 \quad , \quad \frac{\partial f}{\partial x}=0 \quad , \quad \frac{\partial f}{\partial y}=0$$

is a node for a definite integral curve; we ask when this point satisfies moreover

$$\frac{\partial f}{\partial u}=0 \quad ,$$

consequently belongs to $E=0$.

If we differentiate $f=0$ partially with regard to x and y, we find:

$$\left.\begin{aligned} \frac{\partial f}{\partial x}+\frac{\partial f}{\partial u}\frac{\partial u}{\partial x}=0 \\ \frac{\partial f}{\partial y}+\frac{\partial f}{\partial u}\frac{\partial u}{\partial y}=0 \,. \end{aligned}\right\} \text{I}$$

Now, if $\frac{\partial f}{\partial x}=\frac{\partial f}{\partial y}=0$, $\frac{\partial f}{\partial u}$ need of course not be zero, for $\frac{\partial u}{\partial x}$ and $\frac{\partial u}{\partial y}$ may be zero, and the latter is the normal case (cf. the geometrical explanation in § 3). Let us suppose viz. that in a particular case $\frac{\partial f}{\partial u}$ is 0, then we can easily determine another system of curves where this is not the case; we have only to replace the equation $f(x,y,u)=0$, by

$$\varphi(x,y,u)=f(x,y,u)+g(u)=0,$$

in which $g(u)$ represents a function which is zero itself for that particular value of u which produces the nodal curve in the system $f=0$, while its derivative $g'(u)$ is not zero for the same value. It is evident that the system of curves $\varphi=0$ has with $f=0$ the nodal curve in common, because for the u of this point is $\varphi=f$, $\frac{\partial \varphi}{\partial x}=\frac{\partial f}{\partial x}$, $\frac{\partial \varphi}{\partial y}=\frac{\partial f}{\partial y}$; on the contrary $\frac{\partial \varphi}{\partial u}=\frac{\partial f}{\partial u}+g'(u)$, and if $\frac{\partial f}{\partial u}=0$, $\frac{\partial \varphi}{\partial u}\neq 0$.

We arrive, however, at quite different results if the system $f=0$ contains a nodal locus. On this locus y and u are functions of x, because not only one or more points of this locus must be determined by x, but at the same time the values of u, by which the integral curves are indicated for which those points are nodes. And as the values of x, y, and u, which are associated to each other by the locus, satisfy at the same time $f=0$, we can say that for each point of that locus

$$\frac{\partial f}{\partial x}+\frac{\partial f}{\partial y}\frac{dy}{dx}+\frac{\partial f}{\partial u}\frac{du}{dx}=0.$$

If now $\frac{\partial f}{\partial x}$ and $\frac{\partial f}{\partial y}$ are both zero, and if $\frac{dy}{dx} \mathrel{=}\!\!\!|\; \infty$, which can occur only in a few points, and may even there be avoided by rotation of the axes of coordinates, then we must have

$$\frac{\partial f}{\partial u}\frac{du}{dx}=0.$$

Now $\frac{\partial f}{\partial u}=0$ will be the normal case, viz. the nodal locus will as a rule belong to $E=0$; for if this is not so $\frac{du}{dx}$ must be $=0$, and u consequently constant along the locus, which means that the said locus is a particular integral to be reckoned twice. It is not excluded, however, that $\frac{\partial f}{\partial u}$ and $\frac{du}{dx}$ are both zero; in that case too there is a particular integral to be reckoned twice, which now does belong to $E=0$, and the difference between this case and the preceding one where there was also question of a particular integral to be reckoned twice is not particularly striking. The geometrical explanation in the following § will cast sufficient light on this case.

§ 3. If we consider the parameter u as a third coordinate, our equation $f(x,y,u)=0$ represents a surface; the sections $u=$ constant produce, if projected on the xy-plane, the various integral curves. The curve $E=0$ lying in the xy-plane contains apparently all the points of the property that the straight lines, passing through those points parallel to the u-axis, cut the surface in two coinciding points; hence it contains:

1st. the apparent contour of the surface for the point at infinity of the u-axis as lighting point, and this is apparently the singular integral;

2nd. the projection of an eventual double curve or cuspidal curve of the surface, situated in such a way that any plane $u=$ constant cuts it in a certain number of points; the system of curves $f=0$ then contains a locus of nodes or cusps in such a way that each integral curve contains *one* or more of those points;

3rd. the projection of an eventual double or cuspidal curve which is lying in a plane $u=$ constant; in that case *one* integral curve counts double, so that $\frac{du}{dx} = 0$ (see § 2), while at the same time $\frac{\partial f}{\partial u} = 0$;

4th. the projections of eventual conical points of the surface; in this case the two equations I of § 2 are satisfied by $\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial u} = 0$, $\frac{\partial u}{\partial x}$ and $\frac{\partial u}{\partial y} \neq 0$, and the points under discussion are nodes of E.

Generally speaking there are, however, a number of tangent planes to be constructed to the surface perpendicularly to the u-axis; they cut the surface each along a curve with a node in the point of contact, but as this node is not at the same time a node of the surface itself, its projection will in general not lie on E; so we have now integral curves with nodes, not belonging to E; in the equations I of § 2 is $\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial u}{\partial x} = \frac{\partial u}{\partial y} = 0$, but $\frac{\partial f}{\partial u} \neq 0$. And if such a node does belong to E after all, it is because the projecting straight line of the point of contact on the surface touches that surface e.g. in another place, or happens to cut it in a point of a double or cuspidal curve; the node of the integral curve is then, however, a simple point of E.

Finally something else is possible. A tangent plane perpendicular to the u-axis may, after the fashion of the two singular tangent planes of a ring, have an infinite number of points of contact; in that case a certain integral curve counts double, however without there being the slightest cause for belonging to E; for the points of contact on the surface are simple points. We have then $\frac{du}{dx} = 0$, but not as under 3), at the same time $\frac{\partial f}{\partial u} = 0$.

§ 4. Passing on to the partial differential equations we represent the complete integral of $F(x, y, z, p, q) = 0$ by $f(x, y, z, u, v) = 0$; it determines a system of ∞^2 integral surfaces.

Elimination of u and v from the four equations

$$f = 0 \quad , \quad \frac{\partial f}{\partial x} = 0 \quad , \quad \frac{\partial f}{\partial y} = 0 \quad , \quad \frac{\partial f}{\partial z} = 0$$

gives two relations between x, y, z, and so a twisted curve, locus of the nodes of ∞^1 surfaces out of the complete system; this twisted curve does not in general lie on the result of the elimination $E = 0$

of u and v from the equations

$$f=0 \quad , \quad \frac{\partial f}{\partial u}=0 \quad , \quad \frac{\partial f}{\partial v}=0,$$

as appears e.g. at once from the example:

$$x^2+y^2-kz^2-2ax-2by=R^2-2a^2-2b^2,$$

representing a system of hyperboloids of revolution with vertical axes.

If $\frac{\partial f}{\partial x}$, $\frac{\partial f}{\partial y}$, $\frac{\partial f}{\partial z}$ are to be $=0$, then $x=a$, $y=b$, $z=0$ and if this point will lie on $f=0$, then a^2+b^2 must be $=R^2$.

The equation then assumes the form:

$$(x-a)^2+(y-b)^2-kz^2=0,$$

and consequently represents now a cone of revolution with its vertex in $x=a$, $y=b$, $z=0$, and the locus of those vertices is the circle $x^2+y^2=R^2$.

On the other hand we find easily that $E=0$ is represented here by

$$x^2+y^2-2kz^2=2R^2;$$

it appears at once therefore that the circle $x^2+y^2=R^2$ does not lie on E here. This is easy to understand. If we consider x as independent variable, then y, z, u, v become in consequence of the nodal locus functions of x (cf. the analogous reasoning in § 2) and as these functions must satisfy the equation $f=0$, we can write:

$$\frac{\partial f}{\partial x}+\frac{\partial f}{\partial y}\frac{dy}{dx}+\frac{\partial f}{\partial z}\frac{dz}{dx}+\frac{\partial f}{\partial u}\frac{du}{dx}+\frac{\partial f}{\partial v}\frac{dv}{dx}=0.$$

Now for a point of the curve $\frac{\partial f}{\partial x}$, $\frac{\partial f}{\partial y}$, $\frac{\partial f}{\partial z}=0$, so that remains:

$$\frac{\partial f}{\partial u}\frac{du}{dx}+\frac{\partial f}{\partial v}\frac{dv}{dx}=0,$$

from which of course it need not ensue that $\frac{\partial f}{\partial u}=\frac{\partial f}{\partial v}=0$, though on the other hand this is not impossible.

That, however, $\frac{\partial f}{\partial u}=\frac{\partial f}{\partial v}=0$ is a particular, and not the general case, appears as follows (cf. § 2).

By elimination of x, y, z from

$$f=0 \quad , \quad \frac{\partial f}{\partial x}=0 \quad , \quad \frac{\partial f}{\partial y}=0, \quad \frac{\partial f}{\partial z}=0$$

we find a function $g(u,v)$ of u and v, which becomes zero for these systems of values of u and v, which determine an integral surface with a node. Conversely an infinite number of functions

$g(u, v)$ may be determined, which become zero for the said values of u and v, while $\frac{\partial g}{\partial u}$, $\frac{\partial g}{\partial v}$ do not become zero for the same values.

If we consider now the system of surfaces:

$$\varphi(x,y,z,u,v) = f(x,y,z,u,v) + g(u,v) = 0 \quad ,$$

where g represents one of that infinite number of functions then this new system has the same locus of nodes as the old one, while for those nodes $\frac{\partial \varphi}{\partial u}$ and $\frac{\partial \varphi}{\partial v}$ are certainly not zero.

Let there be a nodal locus, formed by a surface; then x and y may both be chosen as independent variables, while z, u, v become functions of them, and as the equation $f = 0$ must always be satisfied, we find by differentiation:

$$\frac{\partial f}{\partial x} + \frac{\partial f}{\partial z} p + \frac{\partial f}{\partial u}\frac{\partial u}{\partial x} + \frac{\partial f}{\partial v}\frac{\partial v}{\partial x} = 0$$

$$\frac{\partial f}{\partial y} + \frac{\partial f}{\partial z} q + \frac{\partial f}{\partial u}\frac{\partial u}{\partial y} + \frac{\partial f}{\partial v}\frac{\partial v}{\partial y} = 0,$$

which equations reduce themselves into the last two terms, as in each point of the double surface $\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z} = 0$. If the determinant

$$\begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial v}{\partial x} \\ \frac{\partial u}{\partial y} & \frac{\partial v}{\partial y} \end{vmatrix} \neq 0,$$

then $\frac{\partial f}{\partial u} = \frac{\partial f}{\partial v} = 0$, and the double surface consequently satisfies $E = 0$; in this case there exists no functional connection between u and v, i. e. the curves $u = \text{const.}$, $v = \text{const.}$ cut each other on the double surface only in a limited number of points, or in other words, each particular integral possesses a finite number of nodes.

Is on the contrary the determinant really zero, then v is a function of u, so that on the double surface the curves $u = \text{const.}$ and $v = \text{const.}$, coincide; there are now only ∞^1 particular integrals possessing nodes, but each of them possesses in that case a double *curve* and its locus is the same surface as just mentioned, which need not, however, belong to $E = 0$, because $\frac{\partial f}{\partial u}$ and $\frac{\partial f}{\partial v}$ need not be zero. They may be zero, though, and in that case the double surface does belong to $E = 0$.

There is still another possibility. It may be that for the whole double surface $u = \text{const.}$, but v not; this, however, is from a geometrical point of view the same case as just mentioned, for $v = \text{const.}$ cuts the double surface now along a curve which is double curve for a definite particular integral. $\frac{\partial f}{\partial v}$ must be zero now, it is true, but $\frac{\partial f}{\partial u}$ must not, so that the double surface need not belong to $E = 0$ either, though on the other hand it is quite possible, as the case $\frac{\partial f}{\partial u} = 0$ is by no means excluded.

A very simple example of a system of surfaces with a double surface not belonging to $E = 0$, gives the equation

$$(x + v)^2 + u(y + u) - z^2 = 0;$$

the double surface is $z = 0$, locus of the secants of the pairs of planes which are found by taking u zero. This plane $z = 0$ does not satisfy, however, the result of elimination E: $y^2 + 4z^2 = 0$.

Finally u as well as v may be constant on the double surface; among the particular integrals there will be *one* in that case, which counts double, and which satisfies $E = 0$ or not, according to for the particular u and v of the double surface $\frac{\partial f}{\partial u}$ and $\frac{\partial f}{\partial v}$ being zero in each point of that surface or not; we have apparently to do then with the singular plane of contact at a surface (see the conclusion of § 3).

To wind up with, it is possible that any point of space is node to some integral surface or other, this will e.g. be so if each integral surface possesses a double curve, and these curves fill the whole space; in that case E disappears identically.

§ 5. In order to illustrate the results of § 4 geometrically we imagine the equation $f(x,y,z,u,v) = 0$ in a space of five dimensions, R_5, interpreted as a twisted four-dimensional variety V_4; for the sake of distinctness we shall call it $V_4(f = 0)$. All points for which $u = \text{const.}$ lie in an R_4, which is perpendicular to the u-axis, and the same holds good for all points $v = \text{const.}$, and these two spaces R_4 cut each other along an R_3, which is absolutely normal to the plane uv, and has a point in common with this plane; this R_3 cuts $V_4(f = 0)$ along a surface π, and if the points of this surface are projected by means of planes parallel to the plane uv on the space R_{xyz} of the x, y and z-axis (by which to each point of π one definite projection is associated), then a surface π', congruent with π arises as projection, because the space of π is parallel with R_{xyz}, and the π' is nothing but a particular integral of the given differential equation.

Through the straight line l_∞ at infinity of the plane uv pass ∞^3 planes; each of them cuts $V_4\,(f=0)$ along a curve, and among them are ∞^2 possessing a node, and whose plane touches therefore the variety. Consequently ∞^2 planes of contact pass through l_∞ touching at $V_4\,(f=0)$; the locus of the points of contact P is therefore a surface Ω, but in general of course a surface that can only occur in an R_5; the projection Ω' of Ω from l_∞ on R_{xyz} is an ordinary surface, which might be called the "apparent contour" of $V_4\,(f=0)$ on R_{xyz}, for the lighting axis l_∞.

The projection of Ω on R_{xyz}, takes place exactly through the planes that have produced Ω itself, viz. the planes of contact passing through l_∞ touching at $V_4\,(f=0)$; now ∞^4 straight lines pass through the point of contact P of such a plane, and consequently ∞^3 that touch at $V_4\,(f=0)$ in P, and they determine the tangent-R_4 in P at $V_4\,(f=0)$; as this tangent-R_4 contains all tangents through P at $V_4\,(f=0)$ it also contains the plane Pl_∞; so it is projecting, the consequence of which is that its projection on R_{xyz}, being nothing but its intersection with R_{xyz}, is only a plane, viz. the plane of contact in P' at Ω'.

Out of point P only one perpendicular line can be let down on the plane uv and through the foot of this perpendicular passes only *one* R_3 absolutely normal to uv, from which it ensues that only one surface π passes through P. The plane of contact at this surface in P coincides by no means with the one at Ω, but does contain tangents of $V_4(f=0)$, as π too belongs to this variety; the plane of contact in P at π lies therefore in the tangent-R_4 of P at $V_4(f=0)$ and so projects itself, as the plane of contact at Ω, in the plane of contact in P' at Ω', from which it ensues that π' and Ω' touch each other in P'; *Ω' is therefore the singular integral of our differential equation.*

In fact Ω' is found analytically by making the (fourdimensional) first polar space $\dfrac{\partial f}{\partial u}=0$ of the point at infinity U_∞ of the u-axis with regard to $V_4\,(f=0)$, and the first polar space $\dfrac{\partial f}{\partial v}=0$ of V_∞, cut each other, in consequence of which the threedimensional first polar space of the line $U_\infty\,V_\infty=l_\infty$ arises; the latter cuts $V_4\,(f=0)$ along the surface Ω, and Ω' satisfies apparently the result of elimination $E=0$ of u and v from $f=0$, $\dfrac{\partial f}{\partial u}=0$, $\dfrac{\partial f}{\partial v}=0$.

§ 6. Among the ∞^2 spaces R_3, which are absolutely normal to the plane $u\,v$, and according to what precedes, cut the surfaces π out of $V_4\,(f=0)$, there are ∞^1 for which that surface of intersection π possesses a node, and which touch V_4 accordingly in that point; this node of π will in general, however, be only a simple point of V_4, i. e. the plane passing through l_∞, and that point will in general cut V_4 along a curve that possesses no node in that point; and from this it ensues that the projection of that point on R_{xyz} will in general not belong to $E=0$. With this we have proved that the nodal curve, which in general is present in our system of surfaces π', will as a rule not belong to $E=0$.

Conversely the possibility is, however, not excluded that $V_4\,(f=0)$ contains a double curve; now the plane passing through l_∞ and a point P of this curve cuts V_4 along a curve which does have a node in P, and the consequence of this is that the projection of the double curve does belong this time to $E=0$; and finally the case is not excluded that both phenomena occur at a time, and consequently the system of surfaces π' contains two different double curves, of which one does belong to $E=0$, the other does not.

Let $V_4\,(f=0)$ contain not a curve but a surface of nodes; as any plane passing through l_∞ and a point P of this double surface cuts $V_4\,(f=0)$ along a curve with a node in P, the projection of the double surface will belong to $E=0$; and as an $R_3 \perp uv$ cuts the double surface in general in a finite number of points we have here to do with the case that each surface of the $\infty^2\pi'$ possesses a finite number of nodes (see § 4).

A double surface in the system π', may, however, have a quite different origin. Among the spaces $R_3 \perp uv$ there may be some that touch $V_4\,(f=0)$ not in *one* but in an infinite number of points, so that the associated surface π possesses a double curve, which, however, is not at the same time a double curve of V_4; in that case there are surfaces π' with a double curve not belonging to $E=0$. And if all $R_3 \perp uv$, which touch V_4, have this property, then we find in the system π' a double surface, locus of double curves of ∞^1 surfaces π', which does not belong to $E=0$. The case is even not excluded that a certain $R_3 \perp uv$ touches $V_4\,(f=0)$ in all the points of a surface, the analogon of the singular planes of contact of a ring, then the differential equation possesses a particular integral counting double, not belonging to $E=0$. If, however, that integral counts double because the associated surface π in R_5 is a real double surface of $V_4\,(f=0)$, which happens to lie in an

$R_3 \perp uv$, then the particular integral counting double does belong again to $E=0$; etc.

Finally V_4 $(f=0)$ may possess a double space, which then is common to the two polar spaces $\frac{\partial f}{\partial u}=0$, $\frac{\partial f}{\partial v}=0$ (cf. § 5). Every $R_3 \perp uv$ cuts this double space along a curve, and every π' contains a double curve, the latter of which fill the whole space R_{xyz} ; the result of the elimination E disappears now identically.

Observation. Following up this method, and without encountering other difficulties but those which arise from the increasing number of dimensions, one can obtain an insight into the singular solution of the partial differential equation of the first order with an arbitrary number of independent variables.

Physics. — *"The diffusion-coefficient of gases and the viscosity of gas-mixtures"*. By Prof. J. P. KUENEN.

(Communicated in the meeting of March 28, 1914).

In a previous communication [1] on the diffusion-coefficient D of gases it was shown, that the contradiction between O. E. MEYER's theory on the one hand and that of MAXWELL-STEFAN-LANGEVIN on the other can be largely removed by taking into account in the former theory the *persistence* of molecular movement. By doing this the limiting values for the two components, i. e. for $n_1=0$ and $n_2=0$, become equal, which involves a much smaller change in D with the composition of the mixture than according to the incomplete theory, while the second theory mentioned makes the coefficient entirely independent of the composition; observation also gives only a small variation of D.

In order to further compare the improved theory with observation I have calculated D for two pairs of gases viz. carbon dioxide—hydrogen and argon—helium, which seemed specially suitable for this test owing to the great difference in the molecular masses. For this purpose it is necessary to give a further modification to the formulae in order to express the influence of the mutual attraction of the molecules: in the former theoretical paper this influence had to be left out of account, seeing that in STEFAN's theory the molecules are likewise regarded as free from attraction.

Using SUTHERLAND's well-known formulation of the attraction by means of a factor $\left(1+\frac{C}{T}\right)$ the formulae become for 0° $(T=273)$.

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[1] J. P. KUENEN, Proc. XV, p. 1152. 1913.

$$l_1 = 1 : \left\{ \sqrt{2}\, n_1 \pi s_1^2 \left(1 + \frac{C_1}{273}\right) + n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273}\right) \right\}$$

$$l_2 = 1 : \left\{ \sqrt{2}\, n_2 \pi s_2^2 \left(1 + \frac{C_2}{273}\right) + n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273}\right) \right\}$$

$$\begin{aligned} f_1 = 1 : \Big\{ 1 - \sqrt{2}\, n_1 \pi s_1^2 \left(1 + \frac{C_1}{273}\right) l_1 \times 0.406 - \\ - n_2 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_2}} \left(1 + \frac{C_{12}}{273}\right) l_1 \frac{m_1 - 0.188 m_2}{m_1 + m_2} \Big\} \end{aligned}$$

$$\begin{aligned} f_2 = 1 : \Big\{ 1 - \sqrt{2}\, n_2 \pi s_2^2 \left(1 + \frac{C_2}{273}\right) l_2 \times 0.406 - \\ - n_1 \pi \sigma^2 \sqrt{\frac{m_1 + m_2}{m_1}} \left(1 + \frac{C_{12}}{273}\right) l_2 \frac{m_2 - 0.188 m_1}{m_1 + m_2} \Big\} \end{aligned}$$

$$D = \frac{1}{3n} \left(n_2 u_1 l_1 f_1 + n_1 u_2 l_2 f_2\right).$$

Possibly in the last formula the coefficient $\frac{1}{3}$ might be replaced by a slightly different one, but the uncertainty involved in this has but a small influence on the result.

A difficulty in the calculation arises from the constant C_{12}, which measures the attraction of unlike molecules. Experiments on the viscosity of mixtures have shown, that the influence of temperature may in that case, as with pure substances, be represented by means of a factor $\left(1 + \frac{C}{T}\right)$; but the constant C in this factor is not identical with the C_{12} in the above formulae, for in the viscosity of a mixture not only the attraction of unlike molecules but also that between like molecules plays a part. If the observations could be represented by a rigorous theoretical formula, the various attractions could be separated and thus the C_{12} in question determined. As this is not the case, however, an estimation has to be resorted to; it seems simplest to take for C_{12} the value which holds for the mixture of composition 1 : 1 as a whole: fortunately a small change in C_{12} does not involve more than a small change in the result.

For the mixture of equal parts of CO_2 and H_2 ($n_1 = n_2 = \frac{1}{2} n$), I have calculated from BREITENBACH's experiments [1]) $C_{12} = 116.2$.

The molecular diameters s_1 and s_2 were found from the viscosities of the pure components at 0° using the formula

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[1]) P. BREITENBACH, Wied. Ann. 67, p. 803, 1899.

$$\eta = 0.44\, d\, u\, l \frac{1}{1+\frac{C}{273}} = \frac{0.44\, d\, u}{\sqrt{2}\, n\, \pi\, s^2 \left(1+\frac{C}{273}\right)},$$

in which n was taken equal to 2.76×10^{19} and further

	d	u	η_0	C
carbon-dioxide	0.00197	36250	0.0001388	239.7
hydrogen	0.0008987	169200	0.0000841	87
mixture	1 : 1		0.0001423	116.2

The result of the calculation is $s_1 = 3.136 \times 10^{-8}$ and $s_2 = 2.217 \times 10^{-8}$, and hence

$$\sigma = \tfrac{1}{2}(s_1 + s_2) = 2.676 \times 10^{-8} .$$

For $n_1 = n_2 = \frac{1}{2} n$ I find $D_{1/2} = 0.453$, whereas the limiting values for pure CO_2 and H_2 become: $D_1 = D_2 = 0.551$. Observation has given $D = 0.53$.

The agreement with observation may be considered satisfactory. The difference between D_{12} and D_1 or D_2 which was discussed in the previous communication, is rather large: probably, as observed, this is owing to the imperfections of the method of calculation by averages followed in the theory.

For argon and helium the following constants hold [1]:

	d	u	η_0	C
Argon	0.001781	38080	0.0002119	164.1
Helium	0.0001784	120400	0.0001819	80.3
Mixture	3 : 2		0.0002207	
,,	1 : 1		0.0002203	105

which give

$$s_1 = 2.674 \times 10^{-8} \quad s_2 = 1.775 \times 10^{-8} \text{ hence } \sigma = 2.224 \times 10^{-8}$$

and

$$D_{1/2} = 0.535 \quad D_1 = D_2 = 0.597 \quad D\,(\text{observed}) = 0.70^{2)}.$$

The agreement with observation is less close here than in the former case; it may be added, that STEFAN's formula (after correction for the molecular attraction) would, as the previous communication shows, give a result closely agreeing with $D_1 = D_2$ according to our formula and therefore also differing from the experimental value.

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1) K. SCHMITT, Ann. d. Phys. (4) 30, p. 393, 1909.

2) R. SCHMIDT. Ann d. Phys. (4) 14 p. 801. 1904. A. LONIUS ib. 29 p. 664 1909.

The further question arises, whether the theory is capable of explaining the viscosity of gas-mixtures, in particular the interesting fact, that, e.g. for the two above combinations, the viscosity goes through a maximum. In order to derive a formula for the viscosity of mixtures it is necessary first to consider the case of a pure substance. The coefficient 0.44 in the formula for η, used above, is the result of the multiplication of the factor 0.35 which is obtained, when the *persistence* is left out of account, and a persistence-factor $\dfrac{1}{1-\dfrac{1}{2}\vartheta}$, where $\vartheta = 0.406$ represents the persistence.

The coefficient $\frac{1}{2}$ in the denominator which is absent in the persistence-factor of the diffusion-formula may be justified as follows [1]). When a molecule is traced on its way from the moment that it collides, it is found, that on the average it does not describe a distance l in the direction of motion, before its velocity in this direction is exhausted and therefore all directions become equally probable, but a distance:

$$l + l\vartheta + l\vartheta^2 + \ldots = \frac{l}{1-\vartheta}.$$

In the case of viscosity however we are dealing with the transport of momentum: it would on the one hand be incorrect to assume, that the momentum of a molecule at each collision immediately assumes the value belonging to the point where the collision occurs; if that were the case, the persistence would have no influence on the viscosity and would have to be left out of account. On the other hand it cannot be assumed, that the molecule keeps its momentum till the moment, when it has lost its velocity in the direction of motion, and then suddenly, as regards momentum, goes into equilibrium with the neighbouring molecules. It is much more reasonable to assume, that at each collision the excess of momentum is equally distributed over the two molecules: on this supposition the persistence-factor will obviously be given by the series

$$1 + \frac{1}{2}\vartheta + \frac{1}{4}\vartheta^2 + \ldots = \frac{1}{1-\frac{1}{2}\vartheta}$$

by which JEANS's result is obtained.

If we now apply this principle to mixtures, it seems natural to suppose, that for collisions between unlike molecules the persistence

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[1]) J. H. JEANS. Theory of gases p. 249—250. 1904.

has to multiplied, instead of by the factor $^1/_2$, by the mass-ratio $\frac{m_1}{m_1+m_2}$ or $\frac{m_2}{m_1+m_2}$ respectively. A rigorous treatment of the problem is impossible, but it would seem that an approximately correct result will be obtained, if in the above formulae for f the first term in the denominator which refers to collisions between like molecules is given the factor $^1/_2$, and the second term which depends on the unlike collisions is multiplied by the aforesaid mass-ratio. In this manner the persistence-factors f' which apply in the case of viscosity assume the following form

$$f'_1 = 1 : \Big\{ 1 - \tfrac{1}{2}\sqrt{2}\, n_1 \pi s_1^2 \left(1 + \frac{C_1}{273}\right) l_1 \times 0.406 -$$

$$- \frac{m_1}{m_1+m_2} \times n_2 \pi \sigma^2 \sqrt{\frac{m_1+m_2}{m_2}} \left(1 + \frac{C_{12}}{273}\right) l_1 \frac{m_1 - 0.188\, m_2}{m_1+m_2} \Big\}$$

$$f'_2 = 1 : \Big\{ 1 - \tfrac{1}{2}\sqrt{2}\, n_2 \pi s_2^2 \left(1 + \frac{C_2}{273}\right) l_2 \times 0.406 -$$

$$- \frac{m_2}{m_1+m_2} \times n_1 \pi \sigma^2 \sqrt{\frac{m_1+m_2}{m_1}} \left(1 + \frac{C_{12}}{273}\right) l_2 \frac{m_2 - 0.188 m_1}{m_1+m_2} \Big\},$$

while the viscosity of the mixture is given by the formula

$$\eta = 0.35 \frac{n_1}{n} d_1 u_1 l_1 f'_1 + 0\ 35 \frac{n_2}{n} d_2 u_2 l_2 f'_2 .$$

For CO_2 and H_2 with $n_1 = n_2 = {}^1/_2 n$ calculation gives $\eta = 0{:}0001482$. The theory therefore actually gives a maximum in the viscosity, in accordance with observation which had not been explained hitherto. The observed maximum lies at $70\,^0/_0$ CO_2 and is not quite so high viz. about 0.000144, but a nearer agreement could not really be expected.

For argon and helium calculation gives

for the mixture 3 : 2 $\eta = 0.0002294$
,, ,, ,, 1 : 1 $\eta = 0.0002321$.

Observation gives a maximum near the first named mixture with $\eta = 0.0002207$; in this case the theory gives again too high a value. Whereas therefore a numerical agreement is absent, we may conclude from the investigation that the ordinary gas theory which treats the molecules as mutually attracting elastic spheres can without being strained explain the occurrence of a maximum in the viscosity of the above mixtures.

Chemistry. — *"The metastable continuation of the mixed crystal series of pseudo components in connection with the phenomenon of allotropy"*. By Prof. A. Smits. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of March 28, 1914).

1. For the case that a unary system is built up of two pseudo-components the relation between the unary and the pseudo-binary system has been derived by me by making use of Gibbs's principle of equilibrium, which states that a system at constant temperature and pressure tends to pass to such a state that the thermodynamic potential (ζ-function) is a minimum. [1]

In this it has been assumed that when heterogeneous allotropy occurs in the solid state, the ζ-x-curve has a shape as indicated in fig. 1. This assumption comes to this that there exists continuity in the unstable region between the two mixed crystal series, which

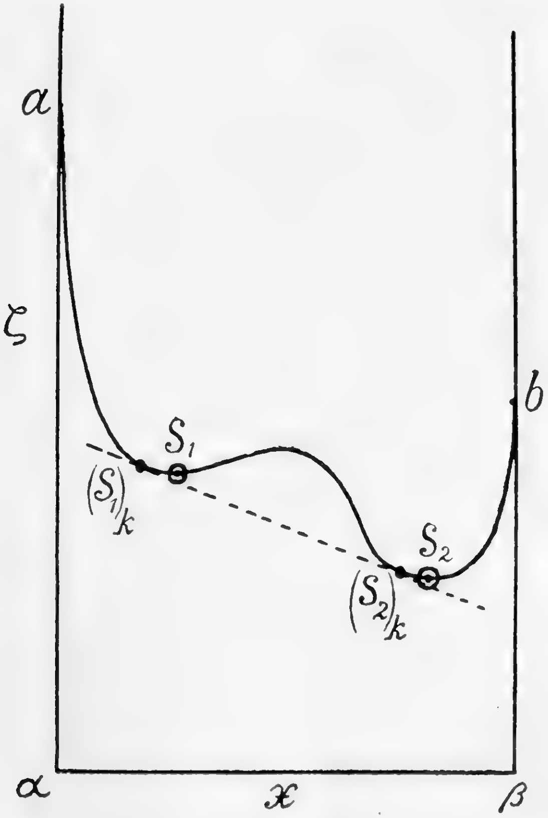

Fig. 1.

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[1] Z. f. phys. Chem.: **76**, 421 (1911).

start from the α and the β-side, and in general possess a different crystalline form.

As HERBETTE [1]) has demonstrated by an experimental way that such a continuous transition between mixed crystals of different crystalline forms occurs for *potassium* and *thallium tartrate* even in the stable region, it must be admitted that the continuity in the unstable region given in fig, 1, is a possibility, especially for mixed crystals whose systems of crystallisation are closely allied to each other.

On the other hand it should be pointed out, that it is very probable, that in many cases the continuity assumed here, does *not* exist, and the two halves of the ζ-x-line, which refer to mixed crystals of different forms, are *not* related. We might imagine that in this case two ζ-x-lines occur, which proceed continuously from one axis to another, as fig. 2 shows. The ζ-x-line *cd* would then relate to mixed crystals of one kind, and *ab* to those of the second kind. The ζ-x-line *cd* then indicates the ζ-values of different mixed crystals, in which the pseudo-component α is compelled by β to crystallize in

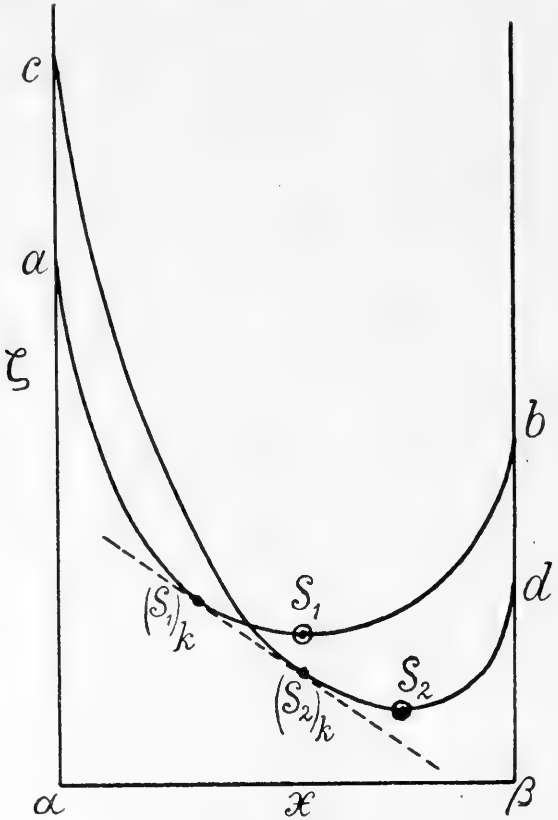

Fig. 2.

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[1]) Compt. rend. **140**, 1649 (1905).

the crystalline form of β, whereas the line ab refers to mixed crystals in which β is forced by α to crystallize in the crystalline form of α.

These states would certainly be realisable when the pseudo components presented the phenomenon of isodimorphy, but then we should have to assume that the pseudo components can occur in different crystalline forms, merely in consequence of a different arrangement in the "Raumgitter" of a same kind of molecules.

Without the slightest doubt such a case is conceivable, but it is by no means probable. We can hardly assume that when the pseudo-components in the solid stable state are miscible to a limited extent, the phenomenon of *isodimorphy* always occurs. *Besides it is in my opinion highly probable that a difference in composition is the cause of the difference in crystalline form.* It is now the question whether another view is possible, which obviates the difficulty mentioned here.

It is clear that the stability of the "Raumgitter" of the pseudo component α becomes smaller as there has been dissolved more of the pseudo component β, and thus it will be possible that at a certain concentration the "Raumgitter" has become so unstable that it can

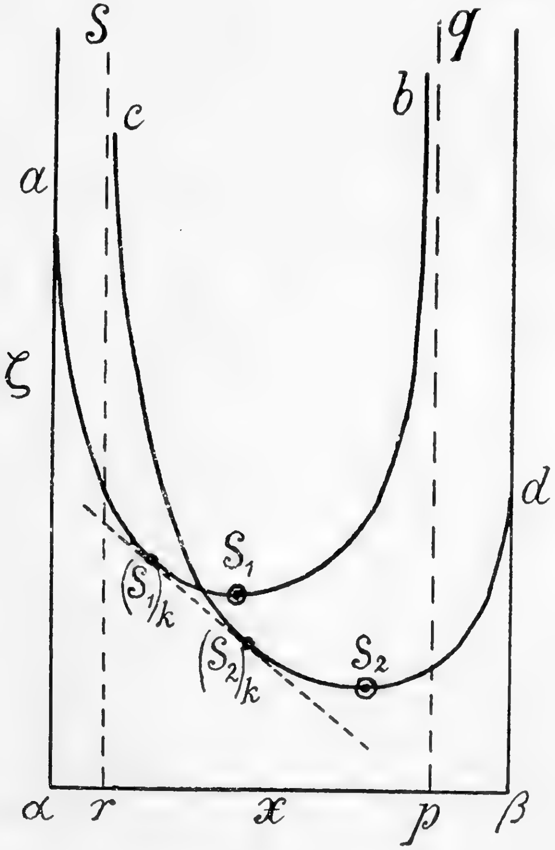

Fig. 3.

no longer maintain itself. It is now the question how this has to be expressed in the ζ-x-figure.

There exist here two possibilities. It is possible that as fig. 3 indicates, the ζ-x-line $a\,b$ starting from the α-axis, approaches the line $p\,q$ asymptotically instead of running to the other axis, which means that a mixed crystal of the concentration p is impossible, as this mixed crystal would require an infinitely large value of ζ.

In the same way the ζ-x-line $d\,c$ would then approach asymptotically to $r\,s$.

Then the expression $\left(\frac{\partial\zeta}{dx}\right)_{PT} = MRT\, log\, \frac{x}{1-x} + \int\limits_{v} \left(\frac{dp}{dx}\right)_{v,\,T} dv$ becomes infinite at a definite value of x, because then the second term of the second member becomes $=\infty$.

Another possibility is this, that the ζ-x-line ends suddenly in the figure, as fig. 4 shows. So this figure expresses that the possibility of the existence of mixed crystals of the same crystalline form suddenly ceases at b resp. c, and that the prolongations of the lines

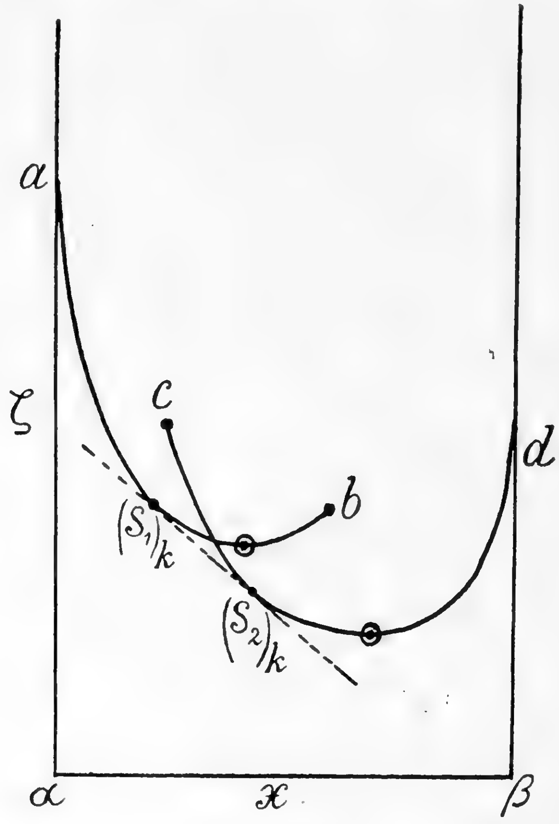

Fig. 4.

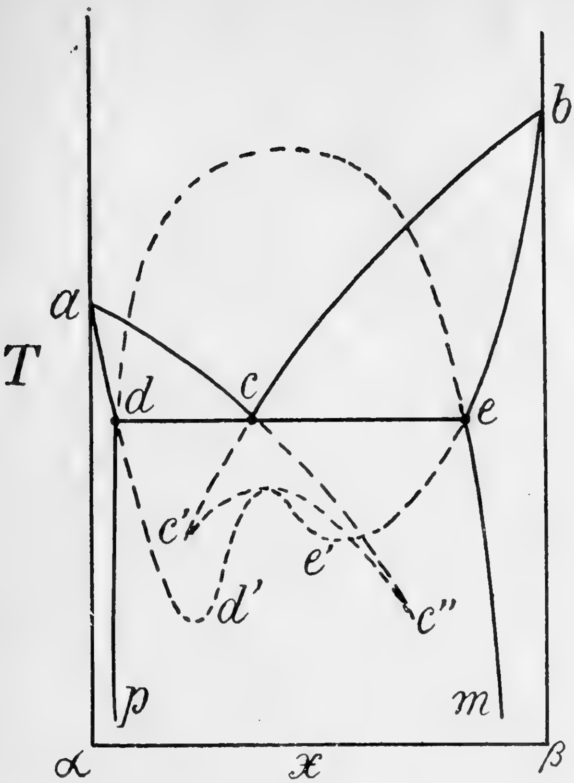

Fig. 5.

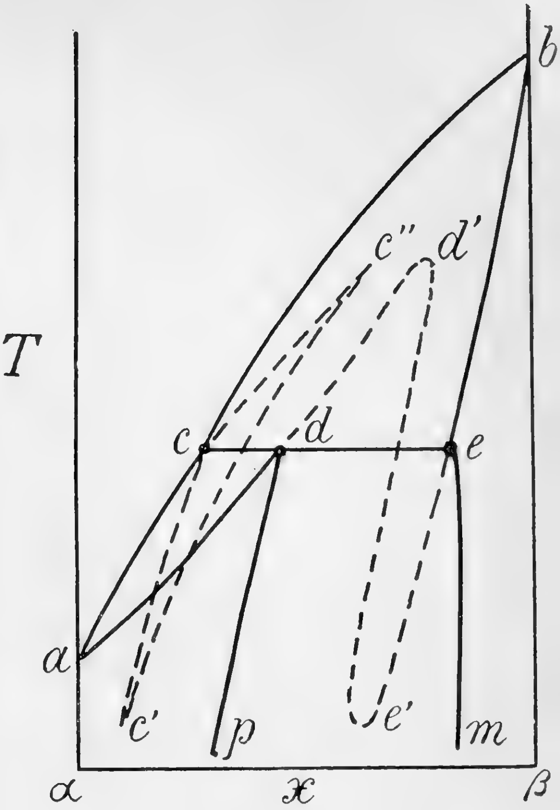

Fig. 6.

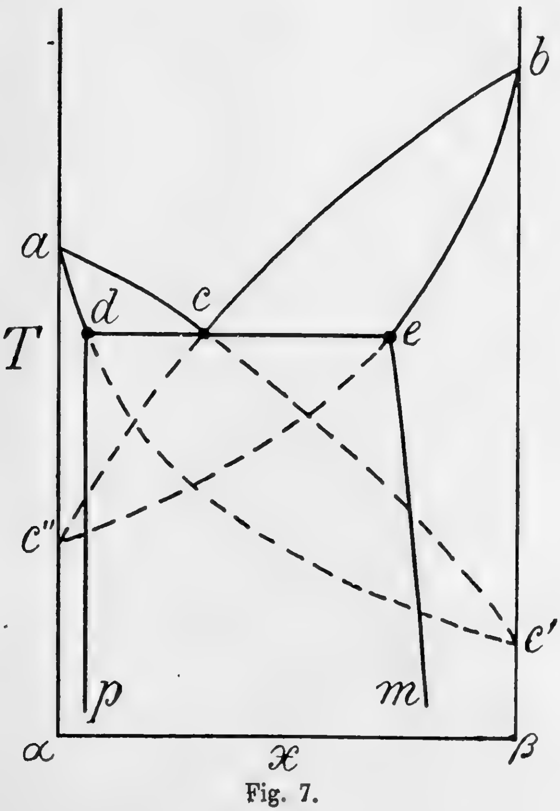

Fig. 7.

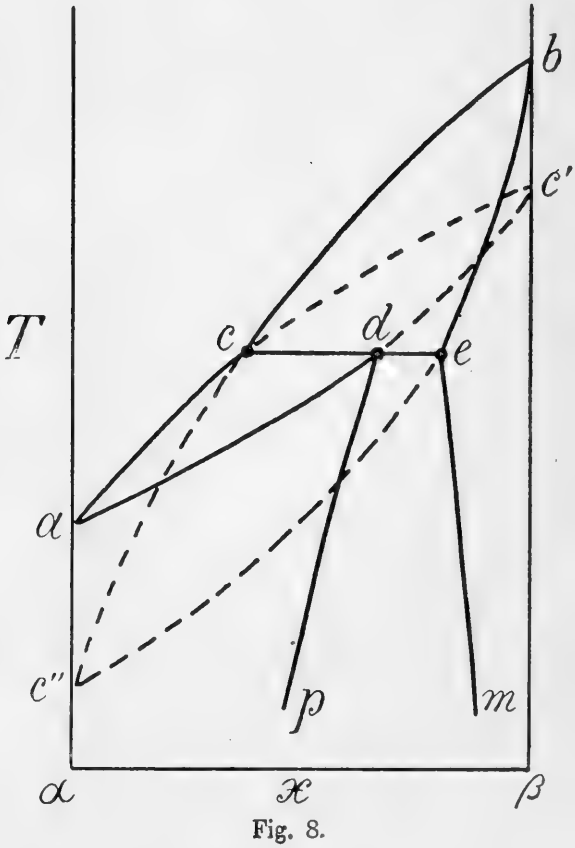

Fig. 8.

which might be imagined, have thermodynamically absolutely no sense any more.

2. It is clear that as far as the metastable and unstable equilibria are concerned, the pseudo T-x-figure will be different according as one view or the other is held.

The assumption of continuity in the unstable region would lead to the T, x-figures 5 and 6.

In Fig. 6 the lines *pd* and *me* pass continuously into each other, in the same way as in Fig. 5.

The assumption of isodimorphy of the pseudo components, which is less probable than the two following, yields the figures 7 and 8.

The assumption of an asymptotic course of the ζ-x-lines leads to the figures 9 and 10.

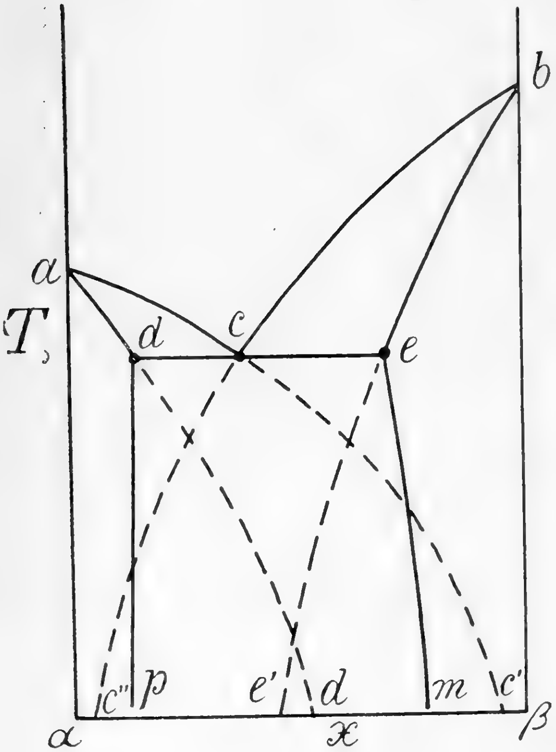

Fig. 9.

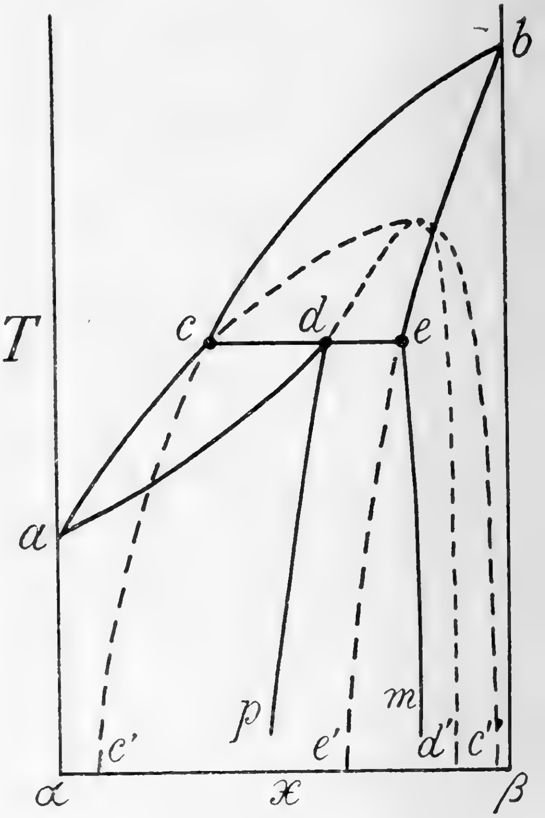

Fig. 10.

$\underset{L}{\left(\frac{\partial^2 \zeta}{\partial x^2}\right)}_{PT}$ becoming $= \infty$ for a definite value of x, and

$$T\left(\frac{dx}{dT}\right)_P = -\frac{\eta_{SL}}{\left(x_S - x_L\right)\underset{L}{\left(\frac{\partial^2 \zeta}{\partial x^2}\right)}_{PT}}$$

$\left(\frac{dx}{dT}\right)_P$ assumes the value *zero* for that definite value of x.

It appears at the same time from these figures that when the temperature of the three phase equilibrium lies between the meltingpoint temperatures of the pseudo-components, one of the metastably produced meltingpoint lines must possess a maximum temperature.

When in conclusion we consider the case that the ζ-x-lines for solid suddenly terminate in the ζ, x-figures, we find what follows for the corresponding T,x-figures.

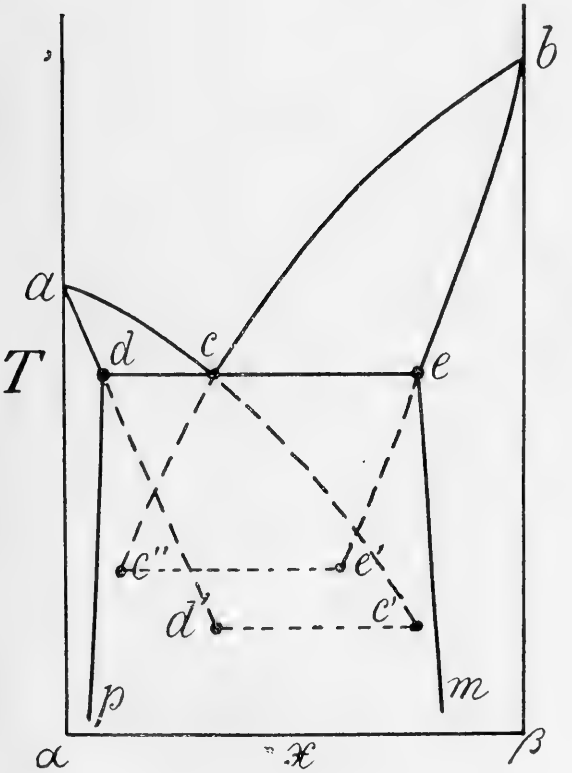

Fig. 11.

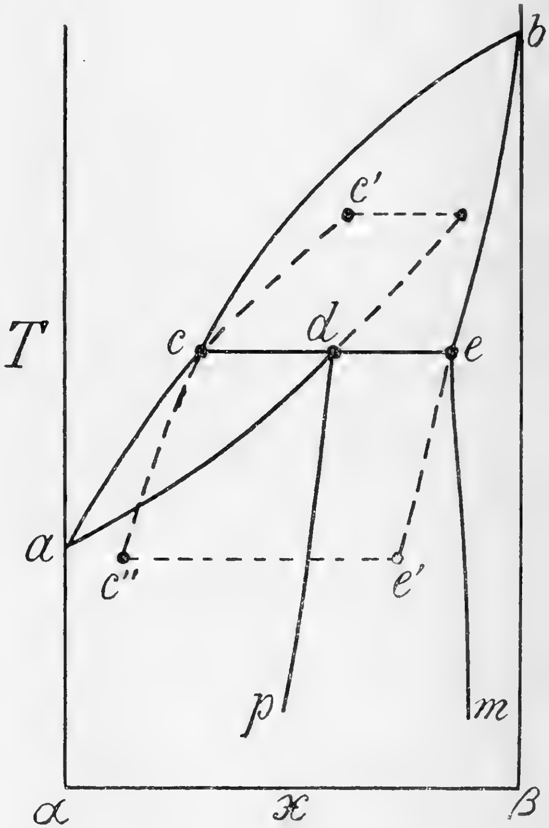

Fig. 12.

We have treated here systems of two pseudo-components α and β, but it is clear, that the same holds also for any other binary system.

Amsterdam, 20 March 1914.

Anorg. Chem. Laboratory of the University.

(To be continued.)

Chemistry. — *"On the vapour pressure lines of the system phosphorus."* I. By Prof. A. Smits, S. C. Bokhorst, and J. W. Terwen. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of March 28, 1913).

1. On a former occasion ¹) the result of a preliminary investigation about the vapour pressure lines of liquid white and liquid red phosphorus was communicated. It appeared already then that the vapour pressure lines of these two colourless liquid phases of the system phosphorus cannot be considered as two pieces of the same vapour pressure line.

The question under discussion being of the utmost importance, which ought to be decided with perfect certainty, it was resolved to determine the vapour pressure lines of liquid white and liquid red phosphorus as accurately and as far as possible.

2. *Determination of the vapour pressure line of liquid red phosphorus.*

We again made use of Jackson's glass spring manometer (see fig. 1 *ab*), which was now made of infusible glass, was filled with pure red phosphorus, and then exhausted and sealed off. This glass spring served as phosphorus reservoir and at the same time as indicator of the pressure.

Round the glass spring a wider vessel *c* had, namely, been sealed on beforehand, which ended into a somewhat narrower tube, which was electrolytically coated with copper at *e*, so that it could be soldered to the copper mounting *e*.

This copper mounting consisted of a copper coupling piece, in which a copper plate was used as packing. The said mounting was in connection with the cocks K_1 K_2 by means of copper tubes, and the pressure cylindre *g*, which was filled with glycerin, and was connected with a Schäffer and Budenberg's hydrostatic press A with closed air manometer M_2, and metal manometer M_3.

The cock K_1 could effect the communication between the space round the glass spring and the carbonic acid cylindre N, and the cock K_2 could bring the same space into communication with the open manometer M_1. A T-piece with the cocks K_3 and K_4 was sealed to this open manometer, K_4 being connected with the Gaede pump. Before the beginning of every experiment the space round the glass spring was exhausted through this cock, to have an opportunity to indicate the zero-position of the needle of the glass spring on the tube *d*. This was effected by sticking two strips of paper

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¹) These Proc. XV, p. 885.

with marks put on them on the front and the back of the tube d, but above each other, in such a way that the two marks are in the same plane with the needle. When a vapour pressure determination was made, a copper bath with a molten mixture of KNO_3 and $NaNO_2$ was placed round the phosphorus manometer, in which a stirrer was continually moved up and down.[1])

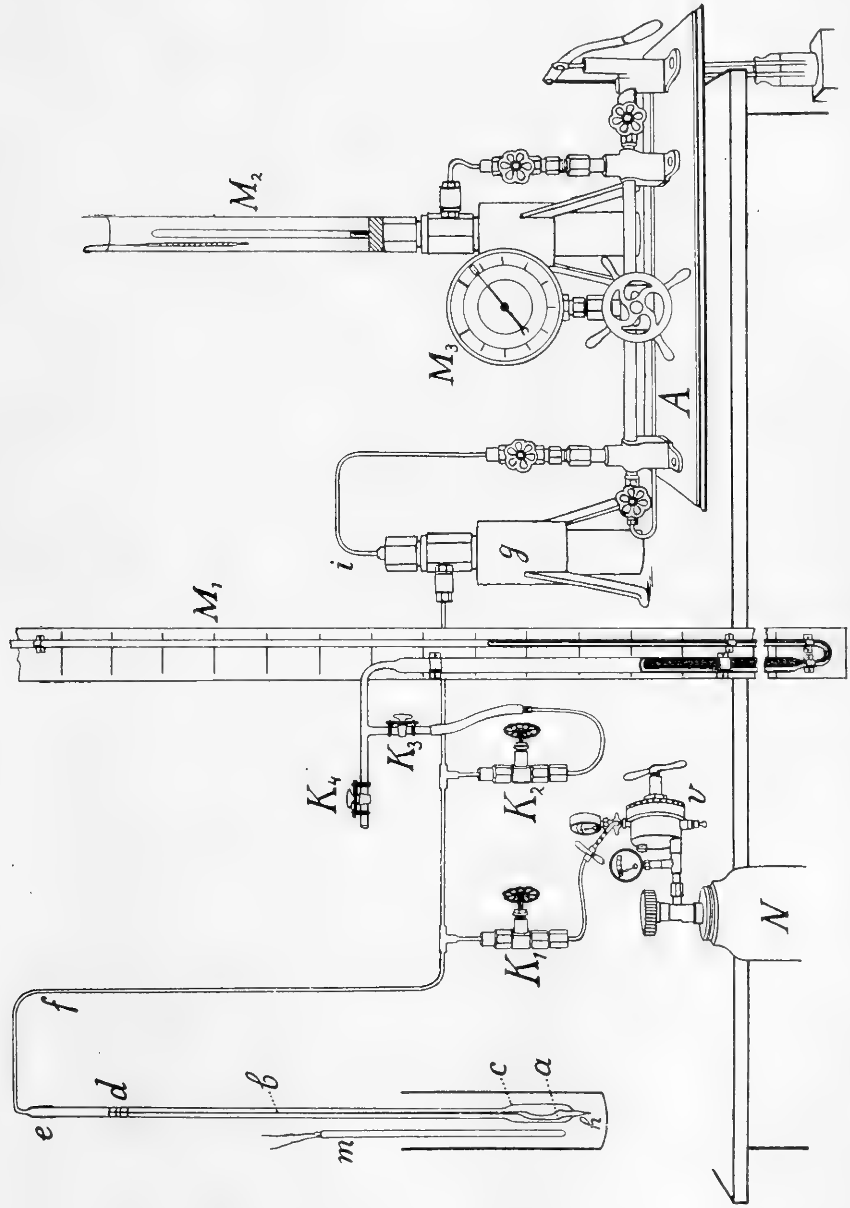

Fig. 1.

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[1]) In the preliminary experiments an air bath was used, with which no accurate determinations could be made, however, on account of the unequal temperature.

Then a gauged thermo-element and a gauged very sensitive resistance thermometer were placed in the bath for the temperature measurement, so that the temperature could be measured in two different ways. The bath was surrounded by a wider asbestos cylindre, burners placed under it ensuring a uniform heating.

In the determination of the vapour pressure line of the liquid red phosphorus the bath was slowly raised to a temperature above the melting point of this modification.

In order to bring the needle of the glass spring manometer to its zero position, the pressure in the space round this manometer had to be continually increased. At first this was effected by slowly admitting air through K_4, K_2 and K_3 being open, but afterwards this was obtained by filling the tube between the valve V and the cock K_1 with CO_2 of higher pressure, after K_4 had been closed, and then carefully opening the cock K_1. As the open manometer could indicate at most an excess of pressure of ± 4 atmospheres, K_2 was closed when this pressure had been reached, so that at higher pressure only the closed air manometer M_2 was used. In its turn the airmanometer was closed at pressures of about 10 atmospheres, and the metal manometer M_3 was read. It had appeared in preliminary experiments that the three different manometers corresponded with each other very satisfactorily.

When the red phosphorus was melted, the temperature was kept constant for some time, the needle was brought exactly to its zero position, and the pressure was read on the air manometer. Then the temperature was slightly raised or lowered; then again put at the same point, and the preceding operation was repeated to get an idea of the accuracy of the method. The result was that the error at these high temperatures and pressures amounted to less than 0,1 atm.

In this way we could determine the vapour pressure line of the molten red phosphorus up to a temperature of 634°, and a pressure of 58.6 atm., which may, indeed, be called a surprising result, for that a glass tube of a diameter of 2 cm. and a thickness of wall of 2 mm. can resist a pressure of 58 atmospheres at a temperature of 634°, was not expected by us, and in these experiments we were fully prepared for a violent explosion, which, however, fortunately did not take place. That the glass had not even been deformed was proved by this that when the experiment was over, the zero position appeared to have hardly changed.

We have been able to continue these vapour tension determinations of the liquid red phosphorus up to ± 85° below the triple point, which lies at **589.5** and **43.1** atm. The supercooled phosphorus then indeed was converted to the solid red phosphorus, but we succeeded in making the experiment in such a way that notwithstanding, the vapour space remained saturate with vapour of the liquid phase during the experiment. The method followed was this,

TABLE I.

$C = 9.609$

$\left(\frac{Q}{R}\right)_{\text{meas.}} = 5031.4$

Number of the manom.	p atm.	t	T	$T \ln p$	$\frac{Q}{R}$	$\Delta \left(\frac{Q}{R}\right)$	calc. p atm.
30	23.2	504	777	2443.0	5023.2	— 8.2	23.0
28	24.3	512	785	2504.5	5038.6	+ 7.2	24.5
27	31.9	545.5	818.5	2834.1	5030.9	— 0.5	31.9
30	32.4	548	821	2855.5	5033.5	+ 2.1	32.5
28	33.0	550	823	2877.6	5030.6	— 0.8	33.0
27	33.6	553	826	2902.9	5034.2	+ 2.8	33.7
28	34.5	555.5	828.5	2934.0	5027.0	— 4.4	34.4
28	35.4	559	832	2967.4	5027.3	— 4.3	35.3
30	35.5	560	833	2973.3	5030.9	— 0.5	35.5
28	35.9	562	835	2989.9	5033.7	+ 2.3	36.0
27	37.6	569	842	3054.0	5036.8	+ 5.4	37.8
28	38.8	574	847	3098.6	5040.2	+ 8.8	39.2
28	40.3	578	851	3145.6	5031.7	+ 0.3	40.3
30	41.1	581	854	3173.4	5032.8	+ 1.4	41.1
28	44.2	593	866	3281.1	5040.4	+ 9.0	44.7
30	47.0	602	875	3368.8	5039.1	+ 7.7	47.4
28	48.6	606.5	879.5	3415.6	5035.6	+ 4.2	48.8
28	49.0	608	881	3428.7	5036.9	+ 5.5	49.3
30	53.9	621	894	3564.5	5026.0	— 5.4	53.6
30	55.6	625.5	898.5	3610.3	5023.5	7.9	55.2
30	56.5	627.5	900.5	3632.7	5020.2	— 11.2	55.9
30	57.7	632	905	3669.9	5026.3	— 5.1	57.4
30	58.6	634	907	3692.2	5023.3	— 8.1	58.1

that for every determination the temperature was raised above the triple point, and then was lowered as quickly as possible to a definite temperature, which was then kept constant for some time, till the vapour tension had become constant. Thus a constant vapour tension could be observed even at the lowest point ± 504° during 5 minutes. On continuation of the experiment pretty suddenly a decrease set in, which pointed to this that at that moment the liquid phase had disappeared, and had been entirely converted to the solid red phosphorus.

That these vapour tensions under the triple point really refer to the saturate vapour could be proved by this that when after the determination of the vapour tension at 550°, the temperature was not first raised above the triple point temperature, but at once to 562°, a vapour tension was observed at this latter temperature, which fitted exactly in the found vapour pressure line. After this determination at 562° we heated at once to 574°, and also the vapour tension observed at this temperature lay on the line already found.

It follows, therefore, from this that the vapour at 562° and 574° was still saturated with the vapour of the liquid red phosphorus, so that it is perfectly sure that this must also have been the case just before and at the lower temperature 550°.

The results of the vapour tension determinations of the liquid red phosphorus are given in the subjoined table. In the first column one finds the number of the manometer, and in the second column the temperature, the third giving the pressure in atmospheres.

In the *PT* representation Fig. 2 these results are graphically represented by the line *cnd*, from which follows that the different observations yield a very regular curve. Only the last point at 512° lies too low.

The point *n* is the point where the vapour pressure line of the solid red phosphorus *mn* (more about this later) intersects the vapour pressure line of the liquid red phosphorus, so the triple point of the red phosphorus.

When the saturation heat is no temperature function, the vapour pressure formula

$$\frac{dlnp}{dT} = \frac{Q}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

on integration yields the expression:

$$lnp = -\frac{Q}{RT} + C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$Tlnp = -\frac{Q}{R} + CT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

from which follows that $Tlnp$, represented as function of T, will yield a straight line.

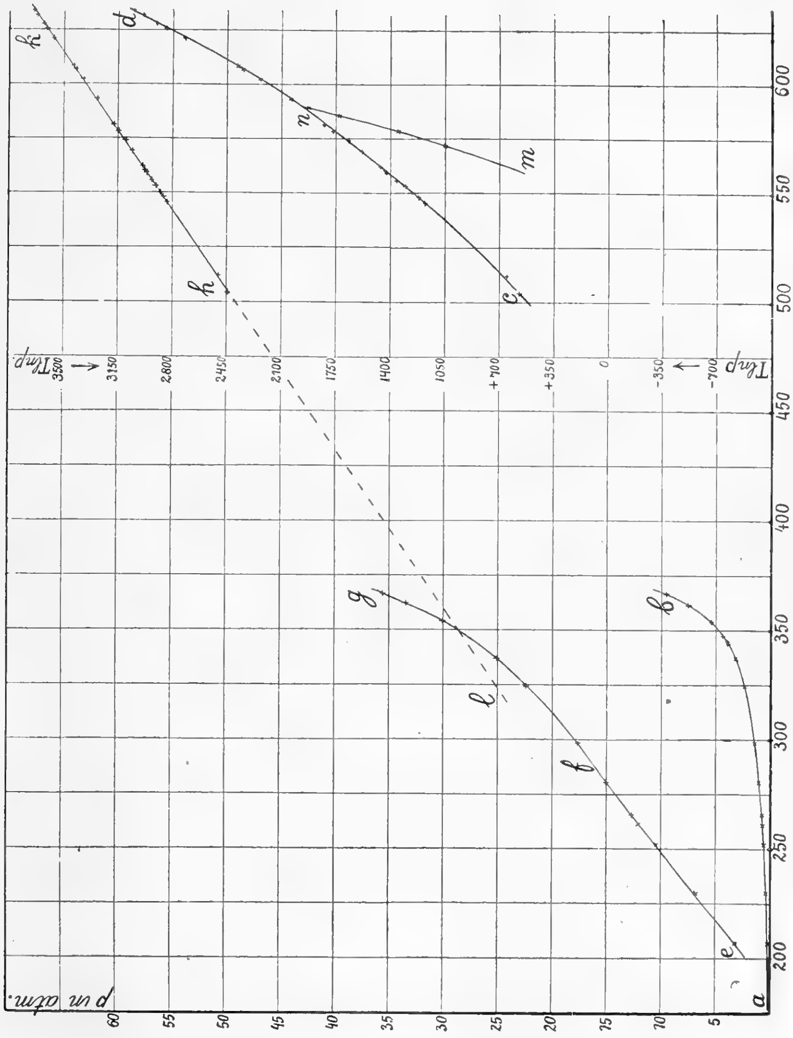

Fig. 2.

It is now interesting to examine what is found when $Tlnp$ is plotted against the temperature.

The points obtained in this way lay so nearly on a straight line that it was possible to unite nearly all the points on the same straight line, as the line hk shows; a proof therefore that the heat of evaporation in the examined temperature range is practically no temperature function.

This has the advantage that the constant C may be graphically determined in a simple way. For this purpose the line is drawn so that as many points as possible lie on this line, and that the others, which deviate lie regularly on the left or the right of it. In this case the tangent of the angle a formed by this line and the temperature axis, will give the constant. This is immediately seen in the following way.

For two different points on this line we get namely:

$$T_1 lnp_1 = -\frac{Q}{R} + CT_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

and

$$T_2 lnp_2 = -\frac{Q}{R} + CT_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

hence

$$C = \frac{T_2 lnp_2 - T_1 lnp_1}{T_2 - T_1} = tg a$$

or

$$C = \frac{2{,}3025(T_2 logp_2 - T_1 logp_1)}{T_2 - T_1} \quad . \; . \; . \; . \; . \; . \quad (6)$$

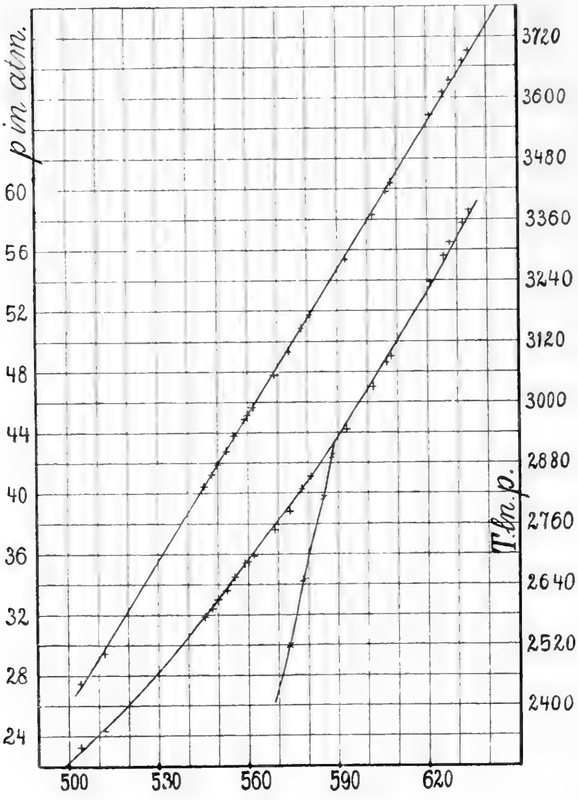

Fig. 3.

In this way the constant C is now determined. If we calculate the quantity $\frac{Q}{R}$ with this value of C from the different observations, we obtain the values given in the 6th column of table I. From this follows as mean value for Q 9,96 K. Cal.

In connection with the deviations from the mean value 5031,4 which the different values of $\frac{Q}{R}$ present (see column 7) it is to be expected that the above value for the heat of evaporation is pretty accurate. Finally the last column gives the calculated pressure when the values for C and $\frac{Q}{R}$ heading the table are used.

To give a better graphical survey of what has been found, the discussed lines are once more separately represented in Fig. 3.

The upmost line again gives $T \ln p$ as function of T.

§ 3. *Determination of the vapour pressure line of liquid white phosphorus.*

If the difficulties in the preceding experiments were great, because many of the glass spring manometers already burst before the triple point of the red phosphorus had been reached, the difficulties in the following experiments were so great as to seem almost insuperable.

It is self-evident that the determination of the vapour tension of the white phosphorus at temperatures at which the conversion to solid red phosphorus still proceeds slowly, is attended with few difficulties.

Up to 312° this line had already been determined by JOLIBOIS [1]) with pretty great accuracy.

For the purpose we had in view, it was, however, necessary to carry these experiments up to as high temperatures as possible. In this we meet, however, with different difficulties. In the first place the molten white phosphorus begins rapidly to convert into the solid red modification from ± 280° on rise of temperature, in consequence of which the liquid phase has disappeared in a comparatively short time, and the prevailing vapour tension, therefore, no longer corresponds with the vapour tension of the liquid phase at that temperature.

Hence to find points of the vapour pressure line of the liquid white phosphorus at higher temperatures, one has to heat the glass spring manometer as quickly as possible to a definite temperature, and then to keep the temperature constant for some time.

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[1]) Thèses, Paris 1910.

By this mode of procedure we have actually succeeded in determining some points with the glass spring manometer at higher temperatures, but in the majority of the experiments the glass spring broke before the required temperature had been reached. This circumstance was owing to this that it often happens in case of rapid heating that part of the liquid white phosphorus is enclosed by a wall of red phosphorus. If now the tension in the space outside has become less than the tension of the enclosed liquid phosphorus, the wall of red phosphorus breaks at a certain difference of pressure, and the consequent sudden increase of pressure bursts the glass spring manometer.

As all attempts to prevent this enclosure of the liquid phosphorus failed, and with a few exceptions the experiments miscarried through this circumstance, we have finally tried to reach our end by another way, in which we have really succeeded. Instead of the statical method we have namely introduced the dynamic method, in the form given to it by SMITH [1]). The difficulty was, however, to find a suitable liquid, i. e. a liquid with a comparatively low melting-point, high boiling-point (± 360°) and besides indifferent with respect to the phosphorus. We have succeeded in finding such a liquid, and to this we owe the final success of our endeavours in this direction. This liquid is melted stearin candle material or a mixture of stearic acid and palmitic acid. Instead of the glass spring manometer the apparatus represented in Fig. 4 was now attached to the apparatus Fig. 1. The former consists of a tube *a*, in which a vessel *c* is placed with a tube *c'*, which is bent downward and part of which is considerably widened, terminating in a capillary placed in a small wider tube. This apparatus, oi which the vessel *c* contains white phosphorus, is quite immersed in the mixture of stearic acid and palmitic acid; and in the same liquid column, at the level of *c* is the extremity of the glass tube *b* fused to at the bottom, in which a thermo-element is placed. The tube *a*, which contains all this, is fastened airtight by means of a rubber stopper in the wider vessel *d*, also provided with the same fatty acid mixture, the side tube *e* of which serves to enable us to compress the air in *d* somewhat, and to raise the boiling point of the mixture, if necessary. By means

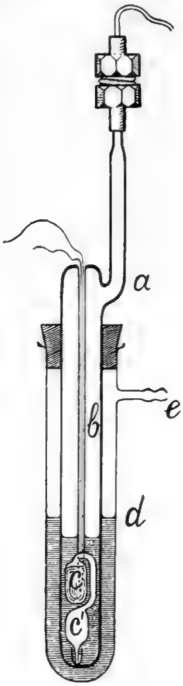

Fig. 4.

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[1]) Americ. Chem. Soc 32, 897 (1910).

of this arrangement it was now possible to determine the boiling-point of the liquid phosphorus under different pressures, and it is in this way that we have supplied the deficiencies which had continued to exist when the static method was applied. The phenomenon of inclosure of liquid phosphorus by solid red also often occurred by this way of procedure with the result that when the wall of the red phosphorus broke, a violent boiling of the liberated liquid took place, in which often part of the contents were flung outside from the vessel *c*.

However satisfactory this dynamic method was in the application, the velocity of conversion of the white phosphorus becomes so great above 360° that 366.4° is the highest temperature at which reliable measurements could still be made.

The result of the statical and the dynamical investigation is combined in the following table II, the results of Jolibois' statical investigation being given in table III.

TABLE II.

Method	Number of the man.	p atm.	t	T	$Tlnp$
dyn.	65	0.039	169.0	442.0	— 1433.9
„	65	0.070	181.3	454.3	— 1208.1
„	65	0.182	206.9	479.9	— 817.6
„	65	0.320	229.8	502.8	— 572.9
„	65	0.542	252.0	525.0	— 321.6
„	65	0.686	261.4	534.4	— 201.4
„	65	0.737	265.5	538.5	— 164.3
stat. and	dyn.	1.—	280.5	553.5	0.0
„	36	1.38	298.6	571.6	+ 184.9
„	35	2.36	324.5	597.5	+ 513.0
„	35	3.18	337.1	610.1	705.8
„	36	3.90	344.9	617.9	840.9
dyn.	54	3.94	343.9	616.9	845.8
„	59	4.38	347.5	620.5	916.5
„	60	5.39	353.9	626.9	1056.0
stat.	31	7.60	362.5	635.5	1291.8
dyn.	56	9.56	366.4	639.4	1443.5

TABLE III.

p atm.	*t*	*T*	*Tlnp*
0.017	145	418	— 1703.1
0.064	173	446	— 1226.0
0.093	184	457	— 1085.4
0.124	192	465	— 970.7
0.157	200	473	— 875.7
0.178	205	478	— 825.0
0.253	219	492	— 676.2
0.366	235	508	— 510.6
0.418	239	512	— 446.6
0.464	244	517	— 397.0
0.499	247	520	— 361.4
0.543	250	523	— 319.4
0.591	254	527	— 277.2
0.633	257	530	— 242.2
0.675	259	532	— 209.1
0.705	262	535	— 187.0
0.797	268	541	— 122.7
0.850	273	546	— 88.7
0.925	275	548	— 42.7
0.990	279	552	— 5.5
1.034	281	554	+ 18.5
1.071	283	556	+ 38.1
1.122	285	558	+ 64.2
1.329	295	568	+ 161.5
1.437	299	572	+ 207.4
1.650	307	580	+ 290.4
1.817	312	585	+ 349.3

Graphically represented the line *ab* Fig, 2 is obtained. As the line *ab* shows, the higher temperatures are the most interesting, for it is from the vapour pressures found at those temperatures that it appears with the greatest clearness that the vapour pressure line of liquid white phosphorus *cannot* be the prolongation of the vapour pressure line of liquid red phosphorus.

This, however, follows still more clearly from the line *efg*, which gives *Tlnp* as function of *T*.

In contrast with the line *hk* this line is *not* straight, but exhibits an ever increasing slope at higher temperatures. So the heat of evaporation is here undoubtedly a decided temperature function, which we shall discuss on a following occasion. The most convincing proof of the lack of correspondence of the vapour tension lines *ab* and *cd* is this that when the line *kh* is prolonged towards lower temperatures, it intersects the line *efg* at a rather large angle, from which it appears still more convincingly than from the lines *ab* and *cd*, that we have here certainly to do with two different curves in the same way as for the system *Cyanogen*.

To set forth still more clearly the regular course of the vapour pressure line *ab*, it has, just as the curve for *Tlnp*, been once more separately represented in Fig. 5. In this figure also the points

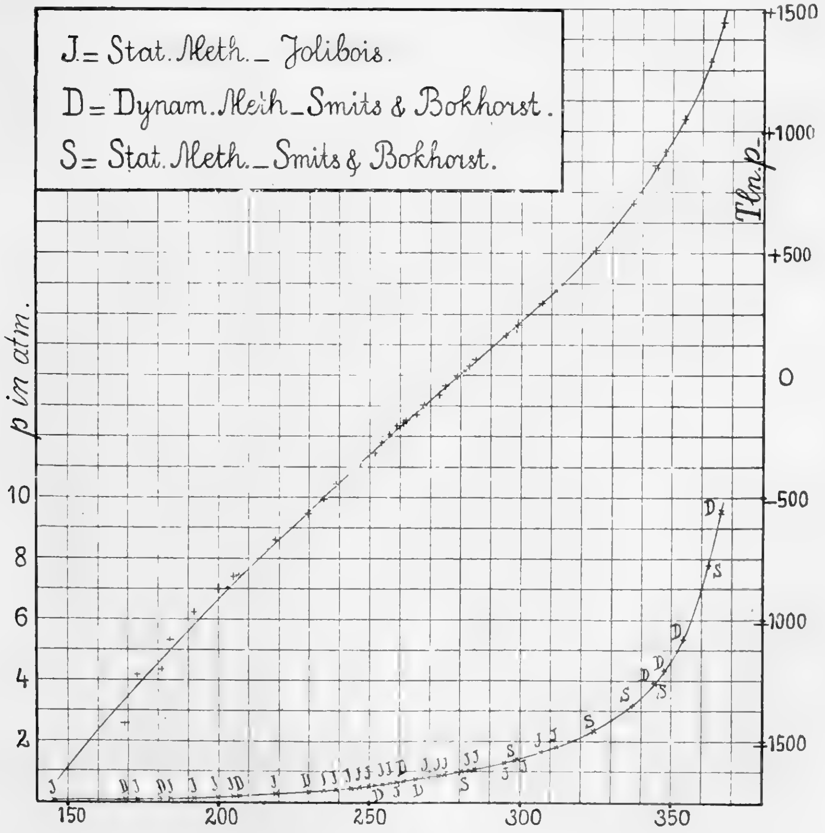

Fig. 5.

determined by JOLIBOIS are indicated, who, as also follows from the table, has only been able to continue his research up to 312°.

In a subsequent communication we shall give some theoretical considerations in connection with the results stated here, and also discuss the vapour pressure line of the solid modification, which we determined accurately already some time ago.

Anorg. Chem. Laboratory of the University.

Amsterdam, March 27, 1914.

Mathematics. — *"A bilinear congruence of rational twisted quartics."* By Professor JAN DE VRIES.

(Communicated in the meeting of March 28, 1914).

1. The base-curves of the pencils of cubic surfaces contained in a net $[\Phi^3]$ form a bilinear congruence. [1])

If all the surfaces of the net have a twisted curve ϱ^5 of genus *one* in common, and moreover pass through two fixed points H_1, H_2, every two Φ^3 cut each other moreover along a rational curve ϱ^4, which rests on ϱ^5 in 10 points. [2])

A third Φ^3 cuts ϱ^4 in 12 points, of which 10 lie on ϱ^5; the remaining 2 are H_1 and H_2. Through an arbitrary point P passes *one* ϱ^4; if P is chosen on a trisecant t of ϱ^5, then all Φ^3 passing through P contain the line t, and ϱ^4 is replaced by the figure composed of t and a τ^3, which cuts it, and meets ϱ^5 in 7 points.

2. In order to determine the order of the ruled surface of the trisecants t, we observe that each point of ϱ^5 bears two trisecants, so that ϱ^5 is nodal curve of the ruled surface (t). We can now prove that a bisecant b, outside ϱ^5, cuts only *one* trisecant, from which it ensues that (t) must be of order five.

The bisecants b, which rest on the bisecant b_0, form a ruled surface (b) of order 7, on which b_0 is a quadruple line. In a plane passing through b_0 lie three bisecants; as to each of those three lines the point of intersection of the other two may be associated, by which a correspondence (1,1) is brought about between the lines b and the points of ϱ^5, (b) is of genus *one*. A plane section of (b) has

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[1]). See my communication in these *Proceedings*, volume XVI, p. 733. There I have considered the case that all Φ^3 have in common a twisted curve ϱ^5 of genus *two*, so that a bilinear congruence of *elliptic* quartics is formed.

[2]). See e.g. STURM, *Synthetische Untersuchungen über Flächen dritter Ordnung* (p.p. 215 and 233).

therefore **14** nodes. Of these 5 lie on ϱ^5, 6 in the quadruple point lying on b_0; the remaining 3 are represented by a triple point originating from a trisecant resting on b_0. As b_0 in each of its points of intersection with ϱ^5 meets two trisecants, (t) is consequently a ruled surface of order *five.* [1])

3. A ϱ^4 cutting ϱ^5 in S forms with it the base of a pencil (Φ^3) the surfaces of which touch in S. We shall now consider two pencils (Ψ) and (Ω) in the net $[\Phi^3]$, and associate to each surface Ψ^3 the surface Ω^3, by which it is touched in S. The pencils having become projective in consequence, produce a figure of order 6, which is composed of the surface Φ^3 common to both pencils and a surface Σ^3. On a line l passing through S a correspondence (2,2) is determined by (Ψ^3) and (Ω); one of the coincidences lies in S, because l is touched in S by two corresponding surfaces. The remaining three are intersections of l with the figure of order 6, mentioned above; the latter has consequently a triple point in S, from which it ensues that S is a node of Σ^3. The curves ϱ^4, which meet ϱ^5 in S, form therefore a cubic surface passing through ϱ^5, which possesses a node in S; ϱ^5 is therefore a *singular curve of order three* for the congruence $[\varrho^4]$.

Through S pass 6 lines of Σ^3; to them belong the two trisecants t, meeting in S; the remaining four are *singular bisecants* of the congruence. Such a line p is cut by ∞^1 curves ϱ^4 in two points, of which one coincides with S, (singular bisecant of the *first kind*).

The ∞^2 rays h, which may be drawn through the *cardinal points* H_1, H_2 possess the same property.

4. An arbitrary line r passing through a point P is cut by *one* ϱ^4 in a pair of points R,R'; the locus of those points is a surface Π of order 5 with triple point P.

If P lies on ϱ^5, then Π^5 consists of the surface Σ^3 belonging to $S \equiv P$ and a quadratic cone, of which the generatrices are *singular bisecants* q. Each line q is bisecant of ∞^1 curves of the $[\varrho^4]$.

If, on the other hand, q is bisecant of a ϱ^4 and at the same time secant of ϱ^5, then the cubic surface passing through ϱ^4, ϱ^5 and q belongs to $[\Phi^3]$; consequently q is cut by the surfaces of this net in the pairs of points of an I^2, is therefore bisecant of ∞^1 curves ϱ^4 (singular bisecant of the *second kind*).

The lines q meeting in a point P, belong to the common gene-

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[1]) Other properties of the ϱ^5 of genus 1 are to be found in my communication "On twisted quintics of genus unity" (volume II, p. 374 of these *Proceedings*).

rators of two cones, which have as curves of direction the ϱ^4 passing through P, and the singular curve ϱ^5. These cones pass through the 10 intersections of ϱ^4 and ϱ^5; of the 15 common generators 5 are lying in lines q. As a plane contains 5 points S, consequently 10 lines q, the *singular bisecants of the second kind* form a congruence (5, 10), which has ϱ^5 as singular curve of the second order.

The cubic cone k^3, which projects a ϱ^4 out of one of its points P, has a nodal line in the trisecant u of ϱ^4, which trisecant passes through P. The latter is at the same time nodal line of the surface Π^5. To the section of Π^5 and k^3 belongs in the first place the curve ϱ^4; further the singular bisecants h_1, h_2, which connect H_1 and H_2 with P, while u represents four common lines; the rest of the section consists of the 5 lines q, which meet in P.

As u with ϱ^4 and ϱ^5 determines a Φ^3, it is cut by the net $[\Phi^3]$ in the triplets of an involution I^3, and is therefore *singular trisecant* of the congruence (common bisecant of ∞^1 curves ϱ^4).

5. Let us now consider the *quadruple involution* (Q^4) in a plane φ, which is determined by the congruence $[\varrho^4]$. It has *five singular points of the third order* in the five intersections S_k of the singular curve ϱ^5. The monoid $\Sigma^3{}_k$ cuts φ along the nodal curve $\sigma^3{}_k$, the points of which are arranged in the triplets of an I^3, which form with S_k quadruples of (Q^4); σ_k also contains the remaining points S (§ 3).

If the point Q describes a line l, the remaining three points Q' of its quadruple describe a curve λ, which passes three times through each of the points S_k. The curves λ and λ^* belonging to l and l^*, have, besides the 45 intersections lying in the points S_k, the three points in common, which form a quadruple with l^*; moreover as many pairs of points as the order of λ indicates. For, if l^* is cut by λ in L^*, then l contains a point L of the quadruple determined by L^*, and the remaining two points belonging to it are intersections of λ and λ^*. The order x of those curves is consequently found from $x^2 = 2x + 48$; hence $x = 8$.

The coincidences of the I^3 on the singular curve $\sigma_1{}^3$ are at the same time coincidences of the (Q^4). Each point S produces two coincidences, the locus γ of the coincidences has therefore in S 6 points in common with $\sigma_1{}^3$; further two in each of the remaining 4 points S and 4 in the coincidences of the I^3. From this it ensues, that the *curve of coincidences* γ is of order six.

(Q^4) consists of the quadruples of base-points of the pencils of cubic curves belonging to a net with the *fixed* base-points S_k. Each point of γ^6 is node of a curve belonging to the net.

6. The transformation (Q,Q') changes a conic into a curve of order 16, with sextuple points in S_k. For the conic τ^2 passing through the five points S, this figure degenerates into the five curves σ^3 and a line u, which contains the triplets of points Q', corresponding to the points Q of τ^2; consequently u is a singular trisecant of $[\varrho^4]$. On the other hand a bisecant u lying in φ is transformed into a figure of order 8, to which u itself belongs twice; as the completing figure must be counted three times and must contain the points S_k, it is the conic τ^2. Consequently φ bears only *one* line u, and the *singular trisecants* of $[\varrho^4]$ form *a congruence* (1,1).

The surface of trisecants of ϱ^5 cuts φ in a curve τ^5 with 5 nodes in S_k. With u, τ^5 has five points T_k in common; each of these points determines a quadruple (Q^4), of which *one* point lies on τ^2, while the remaining two are situated on u. By means of the transformation (Q,Q') τ^5 is therefore changed into a curve of order 10, τ^{10}. The latter is apparently the intersection of φ with the surface formed by the twisted cubics τ^3, which with the trisecants t are associated into degenerate curves of $[\varrho^4]$.

With $\sigma_1{}^3, \tau^5$ has, apart from the singular points S, three points in common; for in S_1 lie 4 intersections and in each of the remaining S, two; therefore S_1 is a triple point on the curve τ^{10}.

The curves τ^3 form therefore a *surface of order ten* with threefold curve ϱ^5.

Of the points of intersection of τ^3 with γ^6, $5 \times 2 \times 2 = 20$ lie in the points S; in each of the remaining 10, a trisecant t is cut by the corresponding cubic curve τ^3. From this it ensues that the locus of the points (t, τ^3) is a *twisted curve of order ten.*

7. The pairs of points Q',Q', which are collinear with a point P, lie (§ 4) on a curve π^5, which passes through the points S_k. If Q describes the line l, QQ' will envelop a curve of class 5. The points Q' describe then (§ 5) a curve λ^8, which passes three times through the points S, consequently has still 25 points in common with π^5; 5 of them connect a point Q' of λ^8 with a point Q of l; the rest form 10 pairs Q',Q''; so that $Q'Q''$ passes through P. From this it ensues that the triplets of the involution $(Q')^3$ lying on λ^8 form triangles which are circumscribed to a curve (*curve of involution*) of class *ten*, $(q)_{10}$.

For a point S_k π^5 degenerates into the curve $\sigma_k{}^3$ and *two singular lines* s_k and $s_k{}^*$ (§ 4); such a line bears an involution I^2 of pairs Q,Q'. A pair is formed by S_k and the intersection of s_k with u;

as the remaining two points 1) of the quadruple lie on u, the pairs Q'',Q''' which complete the pairs Q,Q'' into groups of (Q^4), will lie on a *conic* σ_k^3. As s_k with the curve σ_k^3, apart from S_k, has two points in common, σ_k^2 passes through the four points S_l. In the transformation (Q,Q') s_k corresponds to the figure of order 8, which is composed of s_k itself, σ_k^3 and σ_k^2 counted twice; this figure, as it ought to do, passes three times through the points S.

Every singular line s_k is bitangent of the curve of involution $(q)_{10}$, mentioned above, for it bears two pairs Q',Q'', for which the point Q is intersection of σ_k^2 with l. The singular line u is septuple tangent of $(q)_{10}$; for first l cuts the conic τ^2 in two points, which each determine a triplet of the I^3 lying on u, on account of which u is six times characterized as tangent; but u contains moreover the pair of points Q',Q'' indicated by the intersection Q of u with l.

The curves $(q)_{10}$ and $(q)_{10}^*$ belonging to l and l^* have therefore in common the line u, which represents 49 common tangents and the 10 lines s, which each represent four of those tangents; the remaining 11 we find in the 3 lines indicated by the point ll^* and the 8 which are determined by the intersections of l^* with λ^8 (cf. § 5).

The curves σ_1^3 and σ_2^3 have the points S_3,S_4,S_5 in common and intersect twice in S_1 and S_2, the remaining two intersections V_{12} and V_{12}' form with S_1 and S_2 a quadruple. From this it ensues that through each two points of ϱ^5 passes only *one* curve of $[\varrho^4]$.

The triangles of involution $Q'Q''Q'''$ described in σ_1^3 envelop a curve of class four (for S_1 belongs to two of those triangles); this curve of involution has u as threefold tangent, for u bears a triplet of points forming with S_1 a group of the (Q^4). So u represents nine common tangents of the curves of involution belonging to S_1 and S_2; the line $V_{12}V_{12}'$ is also a common tangent; the remaining six are apparently singular lines s and form three pairs, which respectively pass through S_3,S_4,S_5.

The singular line s_k^* is cut by the conic σ^2_k in two points, which form a quadruple with two points of s_k; so they lie on σ^{*2}_k. Consequently s_k and s_k^* are opposite sides of *one* quadrangle of involution, which has S_1 as adjacent vertex. The two coincidences of the (Q^4) lying in S_1 also determine quadruples, for which S_1 is adjacent vertex. It is easy to see that there are no other quadruples of which two opposite sides intersect in S_1. From this it is evident that an arbitrary point is *adjacent vertex* of *three quadrangles.*

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1). One of those points lies on s_k^* and forms with S_k a pair of the I^2 lying on that line.

8. Let (φ^3) be a pencil belonging to the net $[\varphi^3]$, which is produced by the intersection of the net $[\Phi^3]$ with the plane φ. The locus of the points which have the same polar line with regard to a curve γ^p and the curves of a pencil (φ^n), is a curve ψ of order $2n+p-3$ [1]), hence a curve of order 9, if for γ^p the curve of coincidences γ^6 is taken. In the points S_k ψ^9 like γ^6, has nodes and there the same tangents as γ^6; so the two curves have 30 points in common in S_k. Further both of them pass through the 12 nodes of the pencil $[\varphi^3]$. In each of the remaining 12 common points D, γ^6 is touched by ψ^9, which means that there the curves of a pencil belonging to $[\varphi^3]$ have three-point contact. In (Q^4) occur therefore *twelve* groups, in which every time *three* points have coincided.

In each of the 12 points D, γ^6 is touched by the *complementary curve* γ^{12}, into which γ^6 is transformed by (Q,Q'); the latter is the locus of the pairs of points which complete the coincidences of (Q^4) into quadruples. The figure of order 48, into which γ^6 is transformed, consists of γ^6 itself, of the 5 curves σ_k^3, each counted twice, and the complementary curve; the latter is consequently indeed of order 12. With τ^2 it has four points in common, arising from the 4 coincidences of the I^3 lying on u; the remaining 20 lie in the points S_k. From this it ensues that γ^{12} has *quadruple* points in the 5 singular points S.

In S_k, γ^{12}, and γ^6 have therefore $5 \times 4 \times 2 = 40$ points in common, they further touch in the 12 points D. The remaining 8 intersections arise from quadruples of which twice two points have coincided; so (Q^4) contains *four* groups, which consist each of *two* coincidences.

Mathematics. — "*On* HERMITE'*s functions.*" By Prof. W. KAPTEYN.

(Communicated in the meetings of March 28 and April 24, 1913).

1. The n^{th} derivative of e^{-x^2} may be put in this form, first given by HERMITE

$$\frac{d^n}{dx^n}(e^{-x^2}) = (-1)^n e^{-x^2} H_n(x)$$

where

$$H_n(x) = (2x)^n - \frac{n(n-1)}{1\,!}(2x)^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2\,!}(2x)^{n-4} - \quad . \quad (1)$$

These polynomia satisfy the following relations [2])

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[1]) See e.g. CREMONA-CURTZE, *Einleitung in eine geometrische Theorie der ebenen Curven*, p. 121.

[2]) Exerc. de Tisserand, 1877, p. 26, 27 and 140.

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2}) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\frac{d^2 H_n}{dx^2} - 2x \frac{dH_n}{dx} + 2n\, H_n = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\frac{dH_n}{dx} - 2n\, H_{n-1} = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$H_n - 2x\, H_{n-1} + 2\,(n-1)\, H_{n-2} = 0 \quad . \; . \; . \; . \quad (5)$$

$$\int_{-\infty}^{\infty} H_m(x)\, H_n(x)\, e^{-x^2}\, dx = 0 \qquad m \neq n \quad . \; . \; . \quad (6)$$

$$\int_{\infty}^{\infty} H_n^2(x)\, e^{-x^2}\, dx = 2^n \,.\, n\,!\, \sqrt{\pi} \quad . \; . \; . \; . \; . \quad (7)$$

The object of this paper is to examine these polynomia and the series connected with these, which also satisfy the differential equation (3).

2. To integrate the differential equation (3) by means of definite integrals, put

$$H_n = e^{x^2} z$$

then we have

$$\frac{d^2 z}{dx^2} + 2x \frac{dz}{dx} + 2\,(n+1)\, z = 0\,.$$

To solve this, we assume

$$z = \int_P^Q e^{-xt}\, T\, dt$$

where T is a function of t, and P and Q are constants. The result of this substitution is

$$2\,(t\, T\, e^{-xt})_P^Q + \int_P^Q e^{-xt} \left[-2t \frac{dT}{dt} + (t^2 + 2n)\, T \right] dt = 0\,.$$

Now this equation will be satisfied, if we make

$$T = t^n\, e^{\frac{t^2}{4}}$$

and

$$P = 0 \qquad Q = \pm\, i\,\infty\,.$$

Hence the general integral is

$$z = c_1 \int_0^{i\infty} e^{-xt + \frac{t^2}{4}}\, t^n\, dt + c_2 \int_0^{-i\infty} e^{-xt + \frac{t^2}{4}}\, t^n\, dt$$

c_2 and c_1 being arbitrary constants.

Putting

$$t = iu$$

this takes the form

$$z = \int_0^\infty e^{-\frac{u^2}{4}} u^n \left(A_n \cos xu + B_n \sin xu\right) du.$$

A_n and B_n being again arbitrary constants.

The general integral of

$$\frac{d^2y}{dx^2} - 2x\frac{dy}{dx} + 2ny = 0$$

therefore may be written

$$y = e^{x^2} \int_0^\infty e^{-\frac{u^2}{4}} u^n \left(A_n \cos xu + B_n \sin xu\right) du.$$

Choosing

$$A_n = \frac{(-1)^n}{\sqrt{\pi}} \cos\frac{n\pi}{2} \qquad B_n = \frac{(-1)^{n+1}}{\sqrt{\pi}} \sin\frac{n\pi}{2}$$

we get the particular integral

$$y = \frac{1}{\sqrt{\pi}} e^{x^2} \int_0^\infty e^{-\frac{u^2}{4}} u^n \cos\left(xu - \frac{n\pi}{2}\right) du$$

which for $x = 0$, reduces to

$$y_{x=0} = \frac{\cos\frac{n\pi}{2}}{\sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{4}} u^n du$$

where

$$\int_0^\infty e^{-\frac{u^2}{4}} u^n du = \begin{cases} \dfrac{n!}{\frac{n}{2}!}\sqrt{\pi} \text{ (n even)} \\ \dfrac{1}{2}\left(\dfrac{n-1}{2}\right)! \text{ (n odd)} \end{cases}$$

Now we know that

$$H_n(0) = \begin{cases} (-1)^{\frac{n}{2}} \dfrac{n!}{\frac{n}{2}!} \text{ (n even)} \\ 0 \quad \text{(n odd)} \end{cases} \qquad \dots\dots\dots \quad (8)$$

therefore this particular integral is $H_n(x)$ and we have

$$H_n(x) = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{4}} u^n \cos\left(xu - \frac{n\pi}{2}\right) du \quad . \quad . \quad . \quad (9)$$

Choosing again

$$A_n = \frac{(-1)^n}{\sqrt{\pi}} \sin \frac{n\pi}{2} \qquad\qquad B_n = \frac{(-1)^n}{\sqrt{\pi}} \cos \frac{n\pi}{2}$$

the second particular integral may be written

$$L_n(x) = \frac{1}{\sqrt{\pi}} e^{x^2} \int_0^\infty e^{-\frac{u^2}{4}} u^n \sin\left(xu - \frac{n\pi}{2}\right) du \quad . \quad . \quad (10)$$

3. This second integral satisfies also the relations (4) and (5). For, differentiating, we have

$$L'_n(x) = 2xL_n(x) + \frac{1}{\sqrt{\pi}} e^{x^2} \int_0^\infty e^{-\frac{u^2}{4}} u^{n+1} \cos\left(xu - \frac{n\pi}{2}\right) du$$

$$= 2xL_n(x) - \frac{1}{\sqrt{\pi}} e^{x^2} \int_0^\infty e^{-\frac{u^2}{4}} u^{n+1} \sin\left(xu - \frac{(n+1)\pi}{2}\right) du$$

or

$$L'_n(x) = 2xL_n(x) - L_{n+1}(x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Differentiating again, and remarking that $L_n(x)$ satisfies the differential equation (3), we find

$$(2n+2)\, L_n - 2x\, L_{n+1} + L_{n+2} = 0$$

or, changing n in $n-2$

$$L_n - 2x\, L_{n-1} + 2\,(n-1)\, L_{n-2} = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is in accordance with (5).

If now we substitute the value

$$L_{n+1} = 2x\, L_n - 2n\, L_{n-1}$$

from (12) in (11), we get

$$L_n' = 2n\, L_{n-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which is in accordance with (4).

4. The function $L_n(x)$ may be expanded in series of ascending powers of x.

If n is even, we have

$$L_n(x) = \frac{(-1)^{\frac{n}{2}}}{\sqrt{\pi}} e^{x^2} \int_0^\infty e^{-\frac{u^2}{4}} u^n \sin xu \, du$$

$$= \frac{(-1)^{\frac{n}{2}}}{\sqrt{\pi}} e^{x^2} \sum_0^\infty (-1)^k \frac{x^{2k+1}}{(2k+1)!} \int_0^\infty e^{-\frac{u^2}{4}} u^{2k+n+1} \, du$$

$$= \frac{(-1)^{\frac{n}{2}}}{\sqrt{\pi}} e^{x^2} . 2^n \sum_0^\infty (-1)^k \left(\frac{n+2k}{2}\right)! \frac{(2x)^{2k+1}}{(2k+1)!}$$

or

$$L_{2m}(x) = \frac{(-1)^m}{\sqrt{\pi}} 2^{2m} . m! e^{x^2} \left[2x - (m+1)\frac{(2x)^3}{3!} + (m+1)(m+2)\frac{(2x)^5}{5!} - \dots \right] \quad (14)$$

Proceeding in the same manner if n is odd, we get

$$L_{2m+1}(x) = \frac{(-1)^{m+1}}{\sqrt{\pi}} 2^{2m+1} m! e^{x^2} \left[1 - (m+1)\frac{(2x)^2}{2!} + (m+1)(m+2)\frac{(2x)^4}{4!} - \dots \right] \quad (15)$$

Both these series are converging for all finite values of the variable, and show that

$$L_n(0) = \begin{cases} 0 & (n \text{ even}) \\ \dfrac{(-1)^{\frac{n+1}{2}} 2^n \left(\frac{n-1}{2}\right)!}{\sqrt{\pi}} & (n \text{ odd}) \end{cases} \quad . \quad . \quad . \quad (16)$$

5. Te investigate the value of $L_n(x)$ for large values of x, take the differential equations

$$\frac{d^2 H_n}{dx^2} - 2x \frac{dH_n}{dx} + 2n H_n = 0$$

$$\frac{d^2 L_n}{dx^3} - 2x \frac{dL_n}{dx} + 2n L_n = 0.$$

Multiply the former by L_n the latter by H_n and subtract, so:

$$H_n \frac{d^2 L_n}{dx^2} - L_n \frac{d^2 H_n}{dx^2} - 2x \left(H_n \frac{dL_n}{dx} - L_n \frac{dH_n}{dx} \right) = 0$$

or integrating

$$H_n \frac{dL_n}{dx} - L_n \frac{dH_n}{dx} = C e^{x^2}$$

C, being the arbitrary constant.

Introducing the relations (4) and (13) this may be written

$$2n [H_n L_{n-1} - L_n H_{n-1}] = Ce^{x^2}.$$

If $x = 0$ we have

$$2n\, H_n\, (0)\, L_{n-1}\, (0) = C \ (n \text{ even})$$

$$-\, 2n\, L_n\, (0)\, H_{n-1}\, (0) = C$$

therefore in both cases

$$C = \frac{2^{n+1}\, n!}{\sqrt{\pi}}$$

thus finally

$$H_n\,(x)\, L_{n-1}\,(x) - L_n\,(x)\, H_{n-1}\,(x) = \frac{2^n\,(n-1)!}{\sqrt{\pi}}\, e^{x^2} \quad . \quad . \quad . \quad (17)$$

Now x having a large value, we may write approximately

$$H_n\,(x) \equiv (2x)^n \qquad H_{n-1}\,(x) \equiv (2x)^{n-1}$$

$$L_n\,(x) \equiv \frac{B_n}{x^{n+1}}\, e^{x^2}$$

and therefore

$$L_n\,(x) \equiv \frac{n!}{\sqrt{\pi}}\, \frac{e^{x^2}}{x^{n+1}} \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

6. Summation of some series containing the functions $H_n(x)$. Let

$$\sum_0^\infty (-1)^k \frac{H_{2k}\,(x)\, H_{2k}\,(a)}{(2k)!} = P \quad \text{and} \quad \sum_0^\infty (-1)^k \frac{H_{2k+1}\,(x)\, H_{2k+1}\,(a)}{(2k+1)!} = Q$$

and write H_{2k} and H_{2k+1} as definite integrals by means of (9), then we have

$$P = \frac{1}{\pi}\, e^{x^2+a^2} \int_0^\infty e^{-\frac{v^2}{4}} \cos av dv \int_0^\infty e^{-\frac{u^2}{4}} \cos xu du \sum_0^\infty (-1)^k \frac{(uv)^{2k}}{(2k)!}$$

$$Q = \frac{1}{\pi}\, e^{x^2+a^2} \int_0^\infty e^{-\frac{v^2}{4}} \sin av dv \int_0^\infty e^{-\frac{u^2}{4}} \sin xu du \sum_0^\infty (-1)^k \frac{(uv)^{2k+1}}{(2k+1)!}$$

where

$$\sum_0^\infty (-1)^k \frac{(uv)^{2k}}{(2k)!} = \cos uv \qquad \sum_0^\infty (-1)^k \frac{(uv)^{2k+1}}{(2k+1)!} = \sin uv.$$

Now

$$\int_0^\infty e^{-\frac{u^2}{4}} \cos xu \cos uv du = \tfrac{1}{2} \int_0^\infty e^{-\frac{u^2}{4}} \left[\cos (x+v)\, u + \cos (x-v)\, u\right] du$$

and

$$\int_0^\infty e^{-\frac{u^2}{4}} \sin xu \sin uv du = \tfrac{1}{2}\int_0^\infty e^{-\frac{u^2}{4}} [\cos (x-v) u - \cos (x+v) u] \, du$$

which may be reduced by means of the relation

$$\int_0^\infty e^{-p^2u^2} \cos \lambda pu du = \frac{\sqrt{\pi}}{2p} e^{-\frac{\lambda^2}{4}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (a)$$

In this way we get

$$\int_0^\infty e^{-\frac{u^2}{4}} \cos xu \cos uv du = \frac{\sqrt{\pi}}{2} e^{-x^2-v^2} (e^{2xv} + e^{-2xv})$$

$$\int_0^\infty e^{-\frac{u^2}{4}} \sin xu \sin uv du = \frac{\sqrt{\pi}}{2} e^{-x^2-v^2} (e^{2xv} - e^{-2xv})$$

and

$$P = \frac{1}{2\sqrt{\pi}} e^{\alpha^2} \int_0^\infty e^{-\frac{5v^2}{4}} \cos \alpha v \, (e^{2xv} + e^{-2xv}) \, dv$$

$$Q = \frac{1}{2\sqrt{\pi}} e^{\alpha^2} \int_0^\infty e^{-\frac{5v^2}{4}} \sin \alpha v \, (e^{2xv} - e^{-2xv}) \, dv.$$

To evaluate these integrals we may remark that the relation (a) holds for complex values of λ. Putting therefore $\lambda = a + ib$ and equating the real and imaginary part in both members of the equation, we obtain

$$\left.\begin{aligned} \int_0^\infty e^{-p^2u^2} \cos apu \, (e^{bpu} + e^{-bpu}) \, du &= \frac{\sqrt{\pi}}{p} e^{-\frac{a^2}{4}+\frac{b^2}{4}} \cos \frac{ab}{2} \\ \int_0^\infty e^{-p^2u^2} \sin apu \, (e^{bpu} - e^{-bpu}) \, du &= \frac{\sqrt{\pi}}{p} e^{-\frac{a^2}{4}+\frac{b^2}{4}} \sin \frac{ab}{2} \end{aligned}\right\} \quad . \quad . \qquad (b)$$

which reduce the values of P and Q to

$$P = \frac{1}{\sqrt{5}} e^{\frac{4(\alpha^2+x^2)}{5}} \cos \frac{4\alpha x}{5} = \sum_0^\infty (1)^k \frac{H_{2k}(x) H_{2k}(\alpha)}{(2k)!} \quad . \quad . \quad . \qquad (19)$$

$$Q = \frac{1}{\sqrt{5}} e^{\frac{4(\alpha^2+x^2)}{5}} \sin \frac{4\alpha x}{5} = \sum_0^\infty (-1)^k \frac{H_{2k+1}(x) H_{2k+1}(\alpha)}{(2k+1)!} \qquad (20)$$

Investigating in the same way a second series

$$S = \sum_{0}^{\infty} \frac{\theta^n H_n(n) H_n(\alpha)}{2^n \,.\, n!}$$

where θ represents a value between 0 and 1, we get

$$\frac{\theta^n H_n(x) H_n(x)}{2^n \,.\, n!} = \frac{\theta^n e^{x^2+\alpha^2}}{\pi \,.\, 2^n . n!} \int_0^\infty \!\! \int_0^\infty e^{-\frac{u^2+v^2}{4}} u^n v^n \cos\left(xu - \frac{n\pi}{2}\right) \cos\left(\alpha v - \frac{n\pi}{2}\right) dudv$$

and

$$\sum_{0}^{\infty} \frac{\theta^n H_n(x) H_n(\alpha)}{2^n \,.\, n!} = \frac{1}{\pi} e^{x^2+\alpha^2} \int_0^\infty \!\! \int_0^\infty e^{-\frac{u^2+v^2}{4}} \cos xu \cos \alpha v \sum_{0}^{\infty} \frac{\left(\frac{\theta uv}{2}\right)^{2k}}{(2k)!} dudv$$

$$+ \frac{1}{\pi} e^{x^2+\alpha^2} \int_0^\infty \!\! \int_0^\infty e^{-\frac{u^2+v^2}{4}} \sin xu \sin \alpha v \sum_{0}^{\infty} \frac{\left(\frac{\theta uv}{2}\right)^{2k+1}}{(2k+1)!} dudv$$

$$= \frac{1}{2\pi} e^{x^2+\alpha^2} \int_0^\infty \!\! \int_0^\infty e^{-\frac{u^2+v^2}{4}} \cos xu \cos \alpha v \left(e^{\frac{\theta uv}{2}} + e^{-\frac{\theta uv}{2}}\right) dudv$$

$$+ \frac{1}{2\pi} e^{u^2+\alpha^2} \int_0^\infty \!\! \int_0^\infty e^{-\frac{u^2+v^2}{4}} \sin xu \sin \alpha v \left(e^{\frac{\theta uv}{2}} - e^{-\frac{\theta uv}{2}}\right) dudv.$$

Now, by means of (b), we may write

$$\int_0^\infty e^{-\frac{u^2}{4}} \cos xu \left(e^{\frac{\theta uv}{4}} + e^{-\frac{\theta uv}{2}}\right) du = 2\sqrt{\pi}\, e^{-x^2+\frac{\theta^2 v^2}{4}} \cos \theta xv$$

$$\int_0^\infty e^{-\frac{u^2}{4}} \sin xu \left(e^{\frac{\theta uv}{2}} - e^{-\frac{\theta uv}{2}}\right) du = 2\sqrt{\pi}\, e^{-x^2+\frac{\theta^2 v^2}{4}} \sin \theta xv$$

therefore

$$S = \frac{1}{\sqrt{\pi}} e^{\alpha^2} \int_0^\infty e^{-\frac{(1-\theta^2)v^2}{4}} \cos(\alpha - \theta x)\, v dv \quad . \quad . \quad . \quad . \quad (21)$$

or

$$S = \frac{1}{\sqrt{1-\theta^2}} e^{\alpha^2 - \frac{(\alpha-\theta x)^2}{1-\theta^2}} = \sum_{0}^{\infty} \frac{\theta^n H_n(x) H_n(\alpha)}{2^n \,.\, n!} \quad , \quad . \quad . \quad (22)$$

This result shows that the series is diverging when $\theta = 1$.

7. We shall next determine whether any function whatever of a real variable can be expressed in a series of this form.

$$f(x) = A_0\,H_0(x) + A_1\,H_1(x) + A_2\,H_2(x) + \ldots$$

Supposing this expansion to be possible the coefficients A_n may be found by means of the relations (6) and (7)

$$A_n = \frac{1}{2^n\,.\,n!\,\sqrt{\pi}}\int\limits_{-\infty}^{\infty} e^{-\alpha^2} f(\alpha)\,H_n(\alpha)\,d\alpha.$$

With these values the second member reduces to

$$S = \lim_{\theta=1}\sum_{0}^{\infty}\theta^n\,A_n\,H_n(x) \text{ [1]}$$

where

$$\sum_{0}^{\infty}\theta^n\,A_n\,H_n(x) = \frac{1}{\sqrt{\pi}}\int\limits_{-\infty}^{\infty} e^{-\alpha^2} f(\alpha)\,d\alpha\sum_{0}^{\infty}\frac{\theta^n\,H_n(x)\,H_n(\alpha)}{2^n\,.\,n!}$$

$$= \frac{1}{\pi}\int\limits_{-\infty}^{\infty} f(\alpha)\,d\alpha\int\limits_{0}^{\infty} e^{-\frac{(1-\theta^2)\,\beta^2}{4}}\cos(\alpha-\theta x)\,\beta\,d\beta.$$

Hence

$$S = \lim_{\theta=1}\int\limits_{0}^{\infty} e^{-\frac{(1-\theta^2)\,\beta^2}{4}}\,d\beta\int\limits_{-\infty}^{\infty} f(\alpha)\cos(\alpha-\theta x)\beta\,d\alpha$$

or

$$S = \frac{1}{\pi}\int\limits_{0}^{\infty} d\beta\int\limits_{-\infty}^{\infty} f(\alpha)\cos(\alpha-x)\,\beta\,d\alpha.$$

Now the second member of this equation represents $f(x)$, when this function satisfies the conditions of DIRICHLET between the limits $-\infty$ and $+\infty$. Every function of this kind may therefore be expanded in a series of the functions H.

8. We now proceed to give some examples of this expansion.

I. Let $f(x) = x^p$, then we have

$$x^p = A_0\,H_0 + A_1\,H_1 + A_2\,H_2 + \ldots$$

where

$$A_n = \frac{1}{2^n\,.\,n!}\,\frac{1}{\sqrt{\pi}}\int\limits_{-\infty}^{\infty} x^p\,H_n\,e^{-x^2}\,dx\,.$$

Evidently this integral is zero when $x^p\,H_n$ is an uneven function

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[1] The idea of introducing θ was suggested to me by Prof. P. DEBYE.

or if $n+p$ is an uneven number; the integral vanishes also when $p<n$. Supposing therefore $p+n$ even and $n \leq p$, we have

$$\int_{-\infty}^{\infty} x^p H_n e^{-x^2} dx = (-1)^n \int_{-\infty}^{\infty} x^p \frac{d^n}{dx^n}(e^{-x^2})\, dx$$

$$= (-1)^n \int_{-\infty}^{\infty} x^p \frac{d}{dx}\left(\frac{d^{n-1}}{dx^{n-1}} e^{-x^2}\right) dx$$

$$= (-1)^{n-1}\, p \int_{-\infty}^{\infty} x^{p-1} \frac{d^{n-1}}{dx^{n-1}} e^{-x^2} dx$$

or

$$\int_{-\infty}^{\infty} x^p H_n e^{-x^2} dx = p \int_{-\infty}^{\infty} x^{p-1} H_{n-1} e^{-x^2} dx .$$

Hence

$$\int_{-\infty}^{\infty} x^p H_n e^{-x^2} dx = \frac{p!}{2^{p-n} \frac{p-n}{2}!} \sqrt{\pi}$$

and

$$A_n = \frac{p!}{2^p \frac{p-n}{2}!\, n!}$$

which gives

$$(2z)^p = H_p + \frac{p(p-1)}{1!} H_{p-2} + \frac{p(p-1)(p-2)(p-3)}{2!} H_{p-4} + \dots$$

II. In the second place expanding

$$e^{2\beta x-\beta^2} = A_0 H_0 + A_1 H_1 + A_2 H_2 + \dots$$

the coefficients are given by

$$A_n = \frac{1}{2^n \, . \, n!} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(\alpha-\beta)^2} H_n(\alpha)\, d\alpha .$$

or, putting $\alpha = y+\beta$, by

$$A_n = \frac{1}{2^n \, . \, n!} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-y^2} H_n(y+\beta)\, dy .$$

Now, expanding $H_n(y+\beta)$ by MACLAURIN's theorem we have

$$H_n(y+\beta) = H_n(y) + \beta H_n'(y) + \dots \frac{\beta^n}{n!} H_n^{(n)}(y)$$

where according to (4)

$$H_n'(y) = 2n\,H_{n-1}(y)$$
$$H_n''(y) = 2^2\,n\,(n-1)\,H_{n-2}(y$$
$$\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot\;\cdot$$
$$H_n^{(n)}(y) = 2^n\,.\,n!\,H_0(y)$$

thus

$$H_n(y+\beta)=H_n(y)+2n\,\beta\,H_{n-1}(y)+2^2n(n-1)\frac{\beta^2}{2!}H_{n-2}(y)+\cdot+2^n.n!\frac{\beta^n}{n!}H_0(y).$$

Introducing this value, we get immediately

$$A_n = \frac{\beta^n}{n!\sqrt{\pi}}\int_{-\infty}^{\infty} e^{-y^2}dy = \frac{\beta^n}{n!}$$

and

$$e^{2\beta x-\beta^2} = 1 + \frac{\beta}{1!}H_1(x) + \frac{\beta^2}{2!}H_2(x) + \frac{\beta^3}{3!}H_3(x) + \ldots$$

From this equation several others may be deduced, for instance

$$e^{-2\beta x-\beta^2} = 1 - \frac{\beta}{1!}H_1(x) + \frac{\beta^2}{2!}H_2(x) - \frac{\beta^3}{3!}H_3(x) + \ldots$$

$$e^{-\beta^2}\frac{e^{2\beta x} - e^{-2\beta x}}{2} = 1 + \frac{\beta^2}{2!}H_2 + \frac{\beta^4}{4!}H_4 + \ldots$$

$$e^{-\beta^2}\frac{e^{2\beta x} - e^{-2\beta x}}{2} = \frac{\beta}{1!}H_1 + \frac{\beta^3}{3!}H_3 + \frac{\beta^5}{5!}H_5 + \ldots$$

$$e^{\gamma^2}\cos 2\gamma x = \sum_0^\infty (-1)^k\frac{\gamma^{2k}}{(2k)!}H_{2k}(x)$$

$$e^{\gamma^2}\sin 2\gamma x = \sum_0^\infty (-1)^k\frac{\gamma^{2k+1}}{(2k+1)!}H_{2k+1}(x)$$

III. As a third example we will expand a discontinuous function. Supposing $f(x)=1$ from $x=0$ to $x=1$ and $f(x)=0$ for $1<x<0$, we have

$$f(x) = A_0H_0 + A_1H_1 + A_2H_2 + \ldots$$

where

$$A_n = \frac{1}{2^n\,.\,n!}\frac{1}{\sqrt{\pi}}\int_0^1 e^{-\alpha^2}H_n(\alpha)\,d\alpha.$$

This coefficient may be determined in the following way. Let

$$I_n = \int_0^1 e^{-\alpha^2}H_n(\alpha)\,d\alpha = \int_0^1 (2\alpha H_{n-1} - 2\,(n-1)\,H_{n-2})\,e^{-\alpha^2}d\alpha$$

then

$$\int_0^1 2\alpha e^{-\alpha^2} H_{n-1} d\alpha = -\int_0^1 H_{n-1} d\left(e^{-\alpha^2}\right) = -\left(e^{-\alpha^2} H_{n-1}\right)_0^1 + \int_0^1 e^{-\alpha^2} H'_{n-1}\, d\alpha$$

$$= H_{n-1}(0) - e^{-1} H_{n-1}(1) + 2(n-1) \int_0^1 e^{-\alpha^2} H_{n-2} d\alpha$$

and

$$I_n = H_{n-1}(0) - e^{-1} H_{n-1}(1) \qquad (n > 0)$$

Now $H_{n-1}(0)$ vanishes for odd values of n, therefore

$$I_{2k} = -e^{-1} H_{2k-1}(1) \qquad (k > 0)$$

$$I_{2k+1} = -e^{-1} H_{2k}(1) + H_{2k}(0) \qquad (k \geqq 0)$$

The following relations hold between three successive values of I:

$$I_{2k+1} - 2 I_{2k} + 2(2k-1) I_{2k-1}(0) = 0 \qquad (k > 0).$$

$$I_{2k} - 2 I_{2k-1} + 2(2k-2) I_{2k-2}(0) = (-1)^k 2 \,.\, \frac{(2k-2)!}{(k-1)!} \qquad (k > 1).$$

For

$$I_{2k+1} - 2 I_{2k} + 2(2k-1) I_{2k-1} = H_{2k}(0) + 2(2k-1) H_{2k-2}(0) -$$
$$- e^{-1} \left[H_{2k}(1) - 2 H_{2k-1}(1) + 2(2k-1) H_{2k-2}(1)\right]$$

where the second member vanishes according to (5).

In the same way the second relation may be proved.

From this it is evident that all values of I depend upon the values of I_1 and I_2, and these may be obtained directly for

$$I_2 = \int_0^1 e^{-\alpha^2} (4\alpha^2 - 2)\, d\alpha = -2e^{-1}$$

$$I_1 = \int_0^1 e^{-\alpha^2} 2\alpha\, d\alpha = 1 - e^{-1}.$$

If $x = 0$ or $x = 1$ the expansion does not hold. For these values however we may easily verify that the second member reduces to the value $\frac{1}{2}$.

Taking $x = 0$, the second member reduces to

$$\lim_{\theta=1} \frac{1}{\sqrt{\pi}} \int_0^1 e^{-\alpha^2} d\alpha \sum_0^\infty \frac{\theta^n H_n(0) H_n(\alpha)}{2^n \,.\, n!}$$

or, according to (22), to

$$\lim_{\theta=1} \frac{1}{\sqrt{\pi}} \int_0^1 \frac{1}{\sqrt{1-\theta^2}} e^{-\frac{\alpha^2}{1-\theta^2}} d\alpha \cdot$$

Assuming

$$\frac{\alpha}{\sqrt{1-\theta^2}}=\beta,$$

we have

$$\lim_{\theta=1}\frac{1}{\sqrt{\pi}}\int_0^{\frac{1}{\sqrt{1-\theta^2}}} e^{-\beta^2}\,d\beta=\frac{1}{\sqrt{\pi}}\int_0^{\infty} e^{-\beta^2}\,d\beta=\tfrac{1}{2}\,.$$

In the same way the value for $x=1$ may be found.

SECOND SECTION.

9. Considering the functions

$$\varphi_n(x)=C_n\,e^{-\frac{x^2}{2}}\,H_n(x)$$

and determining the value of the constant C_n so that

$$\int_{-\infty}^{\infty}\varphi_n^2(x)\,dx=1$$

we easily get

$$C_n=\frac{1}{2^{\frac{n}{2}}\sqrt{n!}\,\sqrt[4]{\pi}}$$

and

$$\varphi_n(x)=\frac{1}{2^{\frac{n}{2}}\sqrt{n!}\,\sqrt[4]{\pi}}\,e^{-\frac{x^2}{2}}\,H_n(x)$$

Putting these values in the integral equation

$$\varphi_n(x)=\lambda_n\int_{-\infty}^{\infty}\varphi_n(\alpha)\,K(x,\alpha)\,d\alpha$$

we shall now determine the unknown function $K(x,\alpha)$ and the unknown constant λ_n, which verify this equation.

The expansion II from Art. 8 gave

$$A_n=\frac{1}{2^n\,.\,n!}\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}e^{-(\alpha-\beta)^2}\,H_n(\alpha)\,d\alpha=\frac{\beta^n}{n!}$$

thus, changing β into u,

$$(2u)^n=\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}e^{-(\alpha-u)^2}\,H_n(\alpha)\,d\alpha.$$

Substituting this value in (9) we have

$$H_n(x)=\frac{1}{2^n\pi}e^{x^2}\int_0^\infty e^{-\frac{u^2}{4}}\cos\left(xu-\frac{n\pi}{2}\right)du\int_{-\infty}^\infty e^{-(\alpha-u)^2}H_n(\alpha)\,d\alpha$$

$$=\frac{1}{2^n\pi}e^{x^2}\int_{-\infty}^\infty e^{-\alpha^2}H_n(\alpha)\,d\alpha\int_0^\infty e^{2\alpha u-\frac{5}{4}u^2}\cos\left(xu-\frac{n\pi}{2}\right)du.$$

Changing α into $-\alpha$, this gives

$$H_n(x)=\frac{(-1)^n}{2^n\pi}e^{x^2}\int_{-\infty}^\infty e^{-\alpha^2}H_n(\alpha)\,d\alpha\int_0^\infty e^{-2\alpha u-\frac{5}{4}u^2}\cos\left(xu-\frac{n\pi}{u}\right)du \quad (c)$$

and putting $-u$ instead of u, the same equation leads to

$$H_n(x)=\frac{1}{2^n\pi}e^{x^2}\int_{-\infty}^\infty e^{-\alpha^2}H_n(\alpha)\,d\alpha\int_{-\infty}^0 e^{-2\alpha u-\frac{5}{4}u^2}\cos\left(xu+\frac{n\pi}{2}\right)du$$

which, by the relation

$$\cos\left(xu-\frac{n\pi}{2}\right)=(-1)^n\cos\left(xu+\frac{n\pi}{2}\right)$$

is equivalent with

$$H_n(x)=\frac{(-1)^n}{2^n\pi}e^{x^2}\int_{-\infty}^\infty e^{-\alpha^2}H_n(\alpha)\,d\alpha\int_{-\infty}^0 e^{-2\alpha u-\frac{5}{4}u^2}\cos\left(xu-\frac{n\pi}{2}\right)du\,. \quad (d)$$

Now, adding the equations (c) and (d) we find

$$H_n(x)=\frac{(-1)^n}{2^{n+1}\pi}e^{x^2}\int_{-\infty}^\infty e^{-\alpha^2}H_n(\alpha)\,d\alpha\int_{-\infty}^\infty e^{-2\alpha u-\frac{5}{4}u^2}\cos\left(xu-\frac{n\pi}{2}\right)du$$

where, putting $u=v-\frac{4}{5}\alpha$

$$\int_{-\infty}^\infty e^{-2\alpha u-\frac{5}{4}u^2}\cos\left(xu-\frac{n\pi}{2}\right)du=e^{\frac{4}{5}\alpha^2}\int_{-\infty}^\infty e^{-\frac{5}{4}v^2}\cos\left(xv-\frac{4}{5}\alpha x-\frac{n\pi}{2}\right)dv=$$

$$=e^{\frac{4}{5}\alpha^2}\cos\left(\frac{4}{5}\alpha x+\frac{n\pi}{2}\right)\int_{-\infty}^\infty e^{-\frac{5}{4}v^2}\cos xv\,dv\,.$$

According to formula (a) Art. 6, we obtain therefore

$$\int_{-\infty}^\infty e^{-2\alpha u-\frac{5}{4}u^2}\cos\left(xu-\frac{n\pi}{2}\right)du=\frac{2\sqrt{\pi}}{\sqrt{5}}e^{\frac{4}{5}\alpha^2-\frac{1}{5}x^2}\cos\left(\frac{4}{5}\alpha x+\frac{n\pi}{2}\right)$$

and finally

$$H_n(x) = \frac{1}{2^n\sqrt{5\pi}}\, e^{\frac{4}{5}x^2} \int_{-\infty}^{\infty} e^{-\frac{\alpha^2}{5}}\, H_n(\alpha)\, \cos\left(\frac{4}{5}\,\alpha x - \frac{n\pi}{2}\right) d\alpha\,.$$

Multiplying this equation by $C_n e^{-\frac{x^2}{2}}$ we have

$$\varphi_n(x) = \frac{1}{2^n\sqrt{5\pi}} \int_{-\infty}^{\infty} \varphi_n(\alpha)\, e^{\frac{3(\alpha^2+x^2)}{10}} \cos\left(\frac{4}{5}\,\alpha x - \frac{n\pi}{2}\right) d\alpha$$

thus

$$\lambda_n = \frac{1}{2^n} \qquad K(x,\alpha) = \frac{1}{\sqrt{5\pi}}\, e^{\frac{3(\alpha^2+x^2)}{10}} \cos\left(\frac{4}{5}\,\alpha x - \frac{n\pi}{2}\right).$$

To make $K(x,\alpha)$ independent of n, we distinguish two cases:
1. n even $= 2m$, then

$$\varphi_{2m}(x) = \frac{(-1)^m}{2^{2m}\sqrt{5\pi}} \int_{-\infty}^{\infty} \varphi_{2m}(\alpha)\, e^{\frac{3(\alpha^2+x^2)}{10}} \cos\frac{4}{5}\,\alpha x\, dx$$

$$\lambda_{2m} = \frac{(-1)^m}{2^{2m}} \qquad K_1(x\,.\,\alpha) = \frac{1}{\sqrt{5\pi}}\, e^{\frac{3(\alpha^2+x^2)}{10}} \cos\frac{4}{5}\,\alpha x\,.$$

2. n odd $= 2m+1$, then

$$\varphi_{2m+1}(x) = \frac{(-1)^m}{2^{2m+1}\sqrt{5\pi}} \int_{-\infty}^{\infty} \varphi_{2m+1}(\alpha)\, e^{\frac{3(\alpha^2+x^2)}{10}} \sin\frac{4}{5}\,\alpha x\, d\alpha$$

$$\lambda_{2m+1} = \frac{(-1)^m}{2^{2m+1}} \qquad K_2(x\,,\alpha) = \frac{1}{\sqrt{5\pi}}\, e^{\frac{3(\alpha^2-x^2)}{10}} \sin\frac{4}{5}\,\alpha x.$$

According to the theory of integral equations we know that

$$K_1(x\,.\,\alpha) = \sum_0^{\infty} \frac{\varphi_{2m}(x)\,\varphi_{2m}(\alpha)}{\lambda_{2m}}$$

$$K_2(x\,.\,\alpha) = \sum_0^{\infty} \frac{\varphi_{2m+1}(x)\,\varphi_{2m+1}(\alpha)}{\lambda_{2m+1}}$$

or

$$K_1(x\,,\alpha) = \frac{1}{\sqrt{\pi}}\, e^{-\frac{x^2+\alpha^2}{2}} \sum_0^{\infty} (-1)^m \frac{H_{2m}(x)\, H_{2m}(\alpha)}{(2m)!}$$

$$K_2(x\,,\alpha) = \frac{1}{\sqrt{\pi}}\, e^{-\frac{x^2+\alpha^2}{2}} \sum_0^{\infty} (-1)^m \frac{H_{2m+1}(x)\, H_{2m+1}(\alpha)}{(2m+1)!}$$

which may be verified by the equations (19) and (20).

10. We shall now show that the function

$$\sigma = \frac{H_{n+1}(x) + k\,L_{n+1}(x)}{H_n(x) + k\,L_n(x)}$$

where k is an arbitrary constant, may be developed in a continuous fraction.

Differentiating and eliminating k, the differential equation for σ, takes the form

$$(y_2 z_1 - y_1 z_2)\frac{d\sigma}{dx} + \left(z_1 \frac{dz_2}{dx} - z_2 \frac{dz_1}{dx}\right)\sigma^2 +$$

$$+ \left(z_2 \frac{dy_1}{dx} - y_1 \frac{dz_2}{dx} + y_2 \frac{dz_1}{dx} - z_1 \frac{dy_2}{dx}\right)\sigma + \left(y_1 \frac{dy_2}{dx} - y_2 \frac{dy_1}{dx}\right) = 0$$

where

$$y_1 = H_{n+1}(x) \qquad y_2 = L_{n+1}(x)$$
$$z_1 = H_n(x) \qquad z_2 = L_n(x)$$

According to (17) the coefficients of this equation may be written

$$y_2 z_1 - y_1 z_2 = -2^{n+1}\, n!\, e^{x^2}$$

$$z_1 \frac{dz_2}{dx} - z_2 \frac{dz_1}{dx} = 2n\,(H_n L_{n+1} - H_{n-1} L_n) = 2^{n+1}\, n!\, e^{x^2}$$

$$z_2 \frac{dy_1}{dx} - y_1 \frac{dz_2}{dx} + y_2 \frac{dz_1}{dx} - z_1 \frac{dy_2}{dx} = 2n\,(H_{n-1} L_{n+1} - H_{n+1} L_{n-1}) = -2^{n+2}\, n!\, x e^{x^2}$$

$$y_1 \frac{dy_2}{dx} - y_2 \frac{dy_1}{dx} = 2\,(n+1)\,(H_{n+1} L_n - H_n L_{n+1}) = 2^{n+2}\,(n+1)!\, e^{x^2}$$

thus

$$\frac{d\sigma}{dx} = \sigma^2 - 2x\sigma + 2\,(n+1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

Substituting

$$\sigma = 2x - \frac{2n}{\sigma_1}$$

the function σ_1 satisfies an equation of the same kind viz.

$$\frac{d\sigma_1}{dx} = \sigma_1^2 - 2x\sigma_1 + 2n.$$

Substituting again

$$\sigma_1 = 2x - \frac{2\,(n-1)}{\sigma_2}$$

the transformed equation is

$$\frac{d\sigma_2}{dx} = \sigma_2^2 - 2x\sigma_2 + 2\,(n-1).$$

and so on, until

$$\frac{d\sigma_n}{dx} = \sigma_n^2 - 2x\sigma_n + 2.$$

Putting now

$$\sigma_n = 2x + \frac{1}{\lambda}$$

we have

$$\frac{d\lambda}{dx} + 2x\lambda = -1$$

thus

$$\lambda = e^{-x^2}\left(C - \int_0^x e^{x^2}\,dx\right)$$

C being an arbitrary constant.

Hence

$$\sigma = 2x - \cfrac{2n}{2x - \cfrac{2\,(n-1)}{2x - \cfrac{2\,(n-2)}{2x - \ddots - \cfrac{2}{2x + \cfrac{e^{x^2}}{C-I}}}}} \tag{24}$$

where

$$I = \int_0^x e^{x^2}\,dx.$$

Thus for

$$n=1 \qquad \sigma^{(1)} = 2x - \cfrac{2}{2x + \cfrac{e^{x^2}}{C-I}} = \frac{H_2\,(C-I) + 2xe^{x^2}}{H_1\,(C-I) + e^{x^2}}$$

$$n=2 \qquad \sigma^{(2)} = \;.\;.\;.\;.\;.\;. = \frac{H_3\,(C-I) + (4x^2-4)\,e^{x^2}}{H_2\,(C-I) + 2xe^{x^2}}$$

$$n=3 \qquad \sigma^{(3)} = \;.\;.\;.\;.\;.\;. = \frac{H_4\,(C-I) + (8x^3-20x)\,e^{x^2}}{H_3\,(C-I) + (4x^2-4)\,e^{x^2}}$$

$$n=n \qquad \sigma^{(n)} = \;.\;.\;.\;.\;.\;. = \frac{H_{n+1}\,(C-I) + T_n\,e^{x^2}}{H_n\,(C-I) + T_{n-1}\,e^{x^2}}.$$

The following relation holds between three successive functions T:

$$T_n = 2xT_{n-1} - 2nT_{n-2}.$$

as appears from the substitution of the values of $\sigma^{(n)}$ and $\sigma^{(n-1)}$ in

$$\sigma^{(n)} = 2x - \frac{2n}{\sigma^{(n-1)}}.$$

Putting $x=0$ in this relation, we obtain

$$\left.\begin{aligned} &T_n(0)=(-1)^{\frac{n}{2}}\,2^n\left(\frac{n}{2}\right)! && (n \text{ even})\\ &T_n(0)=0 && (n \text{ odd})\end{aligned}\right\} \quad \ldots\ldots \quad (25)$$

If now we compare the two forms

$$\sigma=\frac{H_{n+1}(C-I)+T_n e^{x^2}}{H_n(C-I)+T_{n-1}e^{x^2}}=\frac{H_{n+1}+kL_{n+1}}{H_n+kL_n} \quad \ldots\ldots \quad (e)$$

we may determine the relation which exists between C and k. For putting $x=0$, we have $I=0$ and

$$\frac{T_n(0)}{C}=kL_{n+1}(0) \quad (n \text{ even})$$

$$\frac{C}{T_{n-1}(0)}=\frac{1}{kL_n(0)} \quad (n \text{ odd})$$

thus

$$k=-\frac{\sqrt{\pi}}{2C}.$$

Therefore if $C=\infty$ the continued fraction (24) represents $\dfrac{H_{n+1}}{H_n}$ and if $C=0$ the value of this fraction is $\dfrac{L_{n+1}}{L_n}$.

From (e) we may deduce a new form for $L_0(x)$. For introducing C instead of k, we have

$$2C\,e^{x^2}\,(H_nT_n-H_{n+1}T_{n-1})-\sqrt{\pi}\,(C-I)\,(H_{n+1}L_n-H_nL_{n+1})-$$
$$-\sqrt{\pi}\,e^{x^2}(L_nT_n-L_{n+1}T_{n-1})=0.$$

Now the relations

$$T_n=2xT_{n-1}-2xT_{n-2}$$
$$H_{n+1}=2xH_n-2nH_{n-1}$$
$$L_{n+1}=2xL_n-2nL_{n-1}$$

lead easily to

$$H_nT_n-H_{n+1}T_{n-1}=2^n\,.\,n\,!$$
$$L_nT_n-L_{n+1}T_{n-1}=2^n\,.\,n\,!\,L_0.$$

With these values, and (17) therefore, we find

$$2C\,.\,2^n\,.\,n\,!-(C-I)\,2^{n+1}n\,!-\sqrt{\pi}\,.\,2^n\,.\,n\,!\,L_0=0$$

or

$$L_0=\frac{2}{\sqrt{\pi}}\,I=\frac{2}{\sqrt{\pi}}\int_0^x e^{x^2}dx \quad \ldots\ldots\ldots \quad (26)$$

This result leads also to a new form for all the functions $L_n(x)$, for

$$L_1 = -\frac{e^{x^2}}{\sqrt{\pi}}\int_0^\infty e^{-\frac{u^3}{4}} u \cos xu\, du = 2xL_0 - \frac{2e^{x^2}}{\sqrt{\pi}}$$

and, according to (12)

$$L_n = H_n L_0 - \frac{2}{\sqrt{\pi}} e^{x^2} T_{n-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where

$$T_{n-1} = H_{n-1} - 2(n-2) H_{n-3} + 2^2(n-3)(n-4) H_{n-5} - \ldots . \quad (28)$$

11. Applying the preceding expansion, the problem of the momenta may be solved.

Let

$$a_n = \int_0^\infty f(y)\, y^n dy$$

the question is to determine the function $f(y)$ when a_n is given for all positive integral values of n.

Putting

$$f(y) = e^{-y^2}[b_0 H_0(y) + b_1 H_1(y) + b_2 H_2(y) + \ldots]$$

we have to determine the coefficients b from

$$a_n = \sum_0^\infty b_p \int_{-\infty}^{\infty} e^{-y^2} y^n H_p(y) dy$$

Here $p+n$ is an even number, for the integral vanishes for $p+n$ odd. Moreover the integral vanishes if $p>n$ therefore

$$a_n = \sum_0^n b_p \int_{-\infty}^{\infty} e^{-y^2} y^n H_p(y) dy$$

or, according to the expansion I Art. 8

$$a_n = n!\sqrt{\pi} \sum_0^n \frac{b_p}{2^{n-p}\frac{n-p}{2}!} .$$

which may be written

$$\frac{a_n}{n!\sqrt{\pi}} = A_n = \sum_0^n \frac{b_p}{2^{n-p}\frac{n-p}{2}!} .$$

Solving these linear equations, we get immediately

$$b_p = \sum_{0}^{\leq \frac{p}{2}} (-1)^k \frac{A_{p-2k}}{2^{2k}\,.\,k!}$$

and accordingly

$$f(y) = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{4}}\, du \sum_0^\infty b_p\, u^p \cos\left(yu - \frac{p\pi}{2}\right)$$

where b_p has the preceding values.

Writing this

$$f(y) = \frac{1}{\sqrt{\pi}} \int_0^\infty e^{-\frac{u^2}{4}}\, du \lfloor \cos yu\ S_1 + \sin yu\ S_2 \rfloor$$

we have

$$S_1 = \sum_{0.2}^{\infty} (-1)^{\frac{p}{2}} b_p u^p$$

$$S_2 = \sum_{1.3}^{\infty} (-1)^{\frac{p-1}{2}} b_p u^p$$

or, expressing b_p in function of the values A

$$S_1 = A_0 - u^2\left(A_2 - \frac{A_0}{2^2 1!}\right) + u^4\left(A_4 - \frac{A_2}{2^2 1!} + \frac{A_0}{2^4\,.\,2!}\right)\dots$$

$$= e^{\frac{u^2}{4}} (A_0 - A_2 u^2 + A_4 u^4 - \dots) = e^{\frac{u^2}{4}} \sum_0^\infty (-1)^k A_{2k} u^{2k}$$

$$= \frac{1}{\sqrt{\pi}} e^{\frac{u^2}{4}} \sum_0^\infty (-1)^k \frac{a_{2k}}{(2k)!} u^{2k}$$

and in the same way

$$S_2 = \frac{1}{\sqrt{\pi}} e^{\frac{u^2}{4}} \sum_0^\infty (-1)^k \frac{a_{2k+k1}}{(2k+1)!} u^{2k+1}\,.$$

therefore

$$f(y) = \frac{1}{\pi} \int_0^\infty du \left[\cos yu \sum_0^\infty (-1)^k \frac{a_{2k}}{(2k)!} u^{2k} + \sin yu \sum_0^\infty (-1)^k \frac{a_{2k+1}}{(2k+1)!} u^{2k+1}\right]$$

or finally

$$f(y) = \frac{1}{\pi} \int_0^\infty \sum_0^\infty (-1)^p \frac{a_p u^p}{p!} \cos\left(yu + \frac{p\pi}{2}\right) du.$$

Of course this is only a formal solution, which holds when the values a_p are such as to make this integral convergent. This is e.g. the case if

$$a_{2k+1} = 0 \qquad a_{2k} = (-1)^k \frac{H_{2k}(1)}{2^{2k}}$$

for then

$$f(y) = \frac{1}{\pi} \int_0^\infty \cos yu \sum_0^\infty \frac{H_{2k}(1)}{(2k)!} \left(\frac{u}{2}\right)^{2k} du$$

or, according to the expansion II

$$f(y) = \frac{1}{2\pi} \int_0^\infty \cos yu \, e^{-\frac{u^2}{4}} (e^u + e^{-u}) \, du,$$

which reduced by b Art. 6, gives

$$f(y) = \frac{e}{\sqrt{\pi}} e^{-y^2} \cos 2y \, .$$

Microbiology. — *"On the nitrate ferment and the formation of physiological species"*. By Prof. Dr. M. W. Beijerinck.

(Communicated in the meeting of March 28, 1913).

It is a well-known fact that in soil as well as in liquids containing a great many individuals of the nitrate ferment, large amounts of organic substances may be present without preventing nitratation, which is the oxidation of nitrites to nitrates by that ferment.

On the other hand it is certain, that when only few germs of the ferment are present, so that they must first grow and multiply in order to exert a perceptible influence, extremely small quantities of organic substance are already sufficient to make the experiments fail altogether, the nitrite then remaining unchanged in the culture media.

It is generally supposed, that this latter circumstance must be explained by accepting that the nitrate ferment can only then grow and increase, when soluble organic substances are nearly or wholly absent.

My own experiments, however, have led me to quite another result, namely that the nitrate ferment very easily grows and increases in presence of the most various organic substances. But in this case, that is, *when growing at the expense of organic food*, it soon wholly loses the power of oxidising nitrites to nitrates and then changes into an apparently common saprophytic bacterium.

This change may be called the formation of a physiological species, and the two conditions of the ferment thus resulting, respectively the *oligotrophic* and the *polytrophic* form.

Furthermore it is proved that the usual laboratory experiments cannot give back to the polytrophic form, when it is kept in absence of soluble organic matter and cultivated in a dilute nitrite solution, the power of oxidising nitrites, not even in the course of 10 years.

Consequently the process of nitratation in pasture ground must take place as follows.

When the soil contains a great deal of organic matter this need not be exclusively oxidised and destroyed by other species of bacteria in order to make the action of the nitrate germs possible, but it may also be done in part of the germs themselves. It is true that they get lost thereby as they pass into the polytrophic form, but in the soil always places must be present without any considerable quantity of organic substance, where unchanged oligotrophic germs occur. These, after the destruction of the organic matter in their environment, can multiply and again provide the soil with a new nitratating flora.

It is very difficult to obtain pure cultures of the nitrate ferment in the nitratating or oligotrophic condition. The best way is as follows. First a crude nitratation is produced by bringing pasture soil into a liquid of the composition: tapwater 100, sodiumnitrite 0,05 to 0,1, bipotassiumfosfate 0,01, and cultivating at 30° C.

After about one or two weeks the nitrate ferment of the infection material has strongly increased and all the nitrite may be converted into nitrate.

A little of this nitratation, diluted with much water, is now sown on the surface of a plate of the composition: tapwater 100, carefully extracted[1]) agar 2, sodiumnitrite 0,05, potassiumfosfate 0,01, and again cultivated at 30° C. As the nitrate ferment and the other microbes accumulating in the crude nitratations, do not attack the agar, the rate of soluble organic food present is very low. The nitrate ferment can grow upon such a plate without losing its faculty of nitratation and forms very minute colonies of about $^1/_2$ to 1 mill. in diameter, which, being very transparent and glassy little discs, are hardly visible. With a greater percentage of water in the agar they are denditrically branched, with a smaller percentage they remain unchanged circular, or become somewhat crenate. In such a pure culture the distance between the colonies must be so great, that they do not touch one another and can be separately examined. In consequence their number on the plates must be relatively small, the counteraction of the still remaining soluble organic substances great, and the nitratative power

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[1]) For the extraction the agar is left many days in distilled water which is now and then renewed.

feeble. Hence the experiment takes much time, two or three weeks or longer.

To obtain pure cultures on silica plates is much more troublesome than on carefully extracted agar, although the nitratation takes place very easily on that medium.

Some other species of bacteria, eventually occurring in the crude nitratations, may produce colonies on the agar much resembling those of the nitrate ferment. Those species which in the crude nitratations do not multiply at all or only very little, are to be recognised on the plates by their relative rarity. But there exists a species, the denitrifying, spore-forming *Bacillus nitroxus* [1]), which can increase in the nitratating fluid and on the plates with the same intensity as the nitrate ferment itself and whose separation from the latter gives rise to difficulties. But here the formation of a new physiological species comes to our assistance, in as much as the nitrate ferment, on broth- or peptone agar, produces very characteristic although no more nitratating colonies. They are white-coloured, extensive and thin; at first dry and flat, they later become thicker, slimy and moist, and are easily distinguished from the small, semi-spherical, moist *Nitroxus* colonies.

On the nitratating plates may further be found the colonies of *Bacillus oligocarbophilus*, which are directly recognised by their white colour and paperlike appearance, and to which I shall return later. Moreover a most characteristic species resembling *Actinomyces*, but in fact nearly allied to *B. oligocarbophilus*. So, in all four species which should be considered as characteristic for the crude nitratations, because, after repeated transplantations they never dissappear, whilst the numerous other species eventually obtained, are but accidental inhabitants and at continued transferring to fresh media may be quite expelled.

When the pure cultures of tbe nitrate ferment are kept in continual contact with the above nitrite solutions, or on the nitrite agar plates poor in soluble organic food, the faculty of oxidising nitrites to nitrates remains unchanged, probably for an unlimited length of time, that is, the ferment preserves its oligotrophic or oligophagic condition. Microscopically it makes the impression of a small *Micrococcus* but in reality consists of very short rodlets of $0,2 \times 0,1\ \mu$, *which in nitratating condition always seem non-motile.*

If the ferment is now transferred to solid media or to culture liquids richer in organic food, as for instance broth agar or agar

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[1]) To compare: Bildung und Verbrauch von Stickoxydul durch Bakterien. Centrabl. für Bakteriologie 2te Abt. Bd. 25, S. 30, 1910.

dissolved in water with $^1/_{20}$ % peptone or more, it grows, as said, vigorously and produces colonies of the above nature, *in which it is always possible to detect some few motile bacteria.* The rodlets now become somewhat longer and thicker than in the nitratating state but for the greater part they remain very short; the ferment has now changed into the polytrophic form.

In broth the same change takes place already on the second or third day, at 30°., fairly rich cultures being obtained, whereby the broth becomes distinctly turbid and is sometimes covered with a thin film, perfectly resembling that of *B. oligocarbophilus.* In the liquid thin rodlets and threads are found, many of which are moving. They never ramify and their motility shows that they do not belong to the family of the Actinomycetaceae, although their way of growing might suggest it. Accordingly the statement in the manuals, that the nitrate ferment may be recognised by its not growing and increasing in pure culture in broth, is quite erroneous, only nitratation is excluded.

On broth-gelatin plates at room temperature the growth is at first rather slow but very characteristic and finally fairly strong, where by the gelatin quite liquefies and much ammonium carbonate is produced.

On pure gelatin, dissolved in distilled water, with nutrient salts, hardly any development is visible, the nitratative power is nevertheless rapidly destroyed.

The quantity of dissolved matter required to destroy this faculty, is extremely small. Media with $^1/_{20}$ % of substances such as glucose, mannite, asparagin, peptone, tyrosin, natriumacetate, or calciumacetate, cause a vigorous growth and total loss of the nitratative function. With a much smaller amount of soluble organic substance in the medium, for example that of common non-extracted agar, the nitrate ferment is able to assimilate that slight quantity without losing the faculty of nitratation. But under these circumstances weeks or months are required for the oxidation of the nitrite, and many experiments fail altogether. Old dung, such as is found in dung-heaps, does not destroy the faculty; vegetable juices, pressed out from stems and roots of plants, convert the nitrate ferment into the polytrophic, non-nitratative form, which conversion must, under certain conditions, also take place in the soil.

Humates in the culture liquids or plates, even in rather great quantities, are not assimilated and cause no change in the nitratation.

Addition of paraffinoil slackens the nitratation a little, but does not at all prevent it.

The very striking fact, that the nitrate ferment acts best when organic substances are as far as possible kept out of the cultures, has suggested the supposition that this microbe could feed by chemosynthesis, whereby the energy, produced by the oxidation of the nitrites should serve for the reduction of atmospheric carbonic acid.

For this hypothesis I have not, however, been able to find a single proof.

When the pure nitrate ferment is cultivated in a liquid this remains quite clear; only with the microscope many bacteria can be detected, especially on the glass wall. A particle of cotton wool fallen from the air into the cultures, represents a quantity of organic matter equalling some millions of nitrate bacteria.

On silica plates soaked with solutions of 0,1°/₀ to 0,05°/₀ sodium nitrite and 1,01°/₀ bipotassium fosfate, the nitrate ferment always forms small but very active colonies only visible when magnified *and the smaller as the organic matter is better removed from the plates.* So there is also here ground to suppose that for the carbon requirement of these extremely small colonies, always a sufficient amount of organic substance is present in the impurities of the plates.

But the strongest argument against the existence of chemosynthesis with regard to the nitrate ferment, is the following circumstance.

The crude cultures are always covered in the laboratory with a thin, floating film, consisting of the above mentioned highly remarkable bacterium, described by me in 1903 under the name of *Bacillus oligocarbophilus*.[1]) When the nitratation experiments are effected in a hothouse this film also appears but later and then it always remains much thinner. When such nitratations are sown out on agar- or silica-plates, *Bacillus oligocarbophilus* likewise forms colonies, which at first sight reveal their relation to the nitrate ferment, but they grow out considerably larger and finally have the appearance of snow-white, dry, flat plates of one or more millimeters in diameter. As *B. oligocarbophilus* is not able to oxidise nitrites, and hence, under the said circumstances does certainly not possess the power of reducing carbonic acid by chemosynthesis, there must evidently be in the environment a sufficient amount of fixed organic carbon to provide the carbon requirement of this species. As the nitrate ferment not only lives in the same fluids as *B. oligocarbophilus,* but by the nature of the colonies resembles it very much, and moreover quite corresponds with it as regards its microscopic appearance, its motility

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[1]) Farblose Bakteriën deren Kohlenstoff aus der atmosferischen Luft herrührt. Centralbl. für Bakteriologie, 2e Abt. Bd. 10. S. 38. 1903.

and its conditions for nutrition in the polyphagous state, it is quite sure that these two bacteria are nearly allied. Consequently we must conclude that the nitrate ferment can feed on the same organic substances, which *B. oligocarbophilus* finds at its disposal, as well in the liquid as in the extracted agar and the silica plates. That those substances are at least partly provided by the atmosphere of the laboratory, I have pointed out in the above mentioned paper.

The nature of these substances is not yet stated, but it is very probable that volatile products, given off by other bacterial cultures occur among them.

In this relation I call to mind the experiment mentioned above with paraffin oil, whose presence does not stop the nitratation. Perhaps the nitrate ferment can feed on it, or on allied substances, whose occurrence in the soil or the atmosphere seems not excluded.

From the foregoing must be concluded, that chemosynthesis for the nitrate ferment is unproved and that, as far as can be judged at present, it is in this case a quite superfluous hypothesis.

Summarising we find, that the nitrate ferment represents a definite state of a greater unity, a physiological species, which may be kept constant in the nearly pure anorganic nitrite solutions, but which, at better nutrition with organic substances, passes into an other state of that unity, another physiological species much more constant.

If the former, that is the nitratating state of the ferment, is called *Nitribacillus oligotrophus,* the latter, non nitratating condition, may be named *Nitribacillus polytrophus.* The conversion of the former into the latter, that is in the direction

N. oligotrophus → *N. polytrophus*

easily takes place; the passage in opposite direction: *N. polytrophus* → *N. oligotrophus*, cannot be effected by the usual laboratory experiments.

Although the nutrition of *Nitribacillus oligotrophus* requires an almost total absence of organic food, there is no cause to ascribe to this ferment the faculty of chemosynthesis.

The question, where the here described case of the formation of a physiological species must be placed in the system of biology, is to be answered as follows.

It cannot be an example of mutation, such as I have amply described for a number of microbes, as the more or less constant products of the mutation process arise at the side of the stock, and continue to exist with it under the most different conditions.

But it is a new case of *hereditary modification,* in fact not much differing from the loss of virulence of many pathogenic bacteria, only much more evident as to the outward characteristics. Comparable to, but not identic, with the pleomorphy of many Fungi; — comparable, too, to the differentiating process in the ontogenetic development of the higher plants and animals, the result of which we observe in the various cell-forms of one and the same individual. By artificial nutrition, and independently of their relation with the other cells, some of these cells can multiply without change of properties, hence, also without returning to the state of the mother-cell or the embryonal cell from which they sprung. The increase of connective tissue and of the muscle cells of the embryonal heart, cultivated in bloodplasm, are good examples.

Finally I wish to remark that the physiological formation of species is not an isolated case for the nitrate ferment, but that it same takes place in the life history of many microbes of soil and water. To these other species, showing the same disposition, belongs *B. oligocarbophilus*, which is, as said, nearly allied to the nitrate ferment itself and on some media cannot even be distinguished from it.

By the isolation of this bacterium on nitrite- or nitrate agar without organic food, the floating films of crude nitratations, colonies are obtained, which by their white, dry surface are perfectly like the films of the culture liquids, and which, when repeatedly transferred on the same medium, without other organic food, can preserve the film-character unchanged in the course of years. But if these cultures are transferred to broth- or peptone agar, their characteristic appearance gets lost, wet and glittering colonies arise, semi-spherical, not extending sideways and seemingly belonging to quite another species. When multiplying they, hereditarily transmit their newly acquired properties, *also when again transplanted on media without organic food.*

The thus obtained polytrophic form and the oligotrophic mother-form, make a couple, quite comparable to the two conditions of the nitrate ferment.

For a long time I considered the polytrophic form of *B. oligocarbophilus* as a wholly different species, always mixed with the primitive stock as an impurity. Erroneously I thought, that the isolation could only be effected by means of a better nutrition, the oligotrophic form thereby dying off. So, I had fallen into the same error as my predecessors concerning the nitrate ferment, but the recognition of the physiological formation of species now brings the required light.

(May 29, 1914.)

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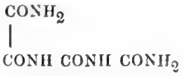

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